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(71)Applicant : NISSAN MOTOR CO LTD
(72)Inventor : YAMAMOTO SHINJI

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(54) EXHAUST GAS CLEANING CATALYST

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an exhaust gas cleaning catalyst with which NOx can be cleaned with high efficiency by using H2 as a reducing agent under an oxygen-excess atmosphere, an HC component and CO component to be not cleaned and discharged in a usual catalyst can be reduced and particularly the HC component can be remarkably reduced in a low temperature region just after an engine is started and which gives highly fuel-efficient effect.
SOLUTION: This catalyst is obtained by layering a zeolite-containing HC adsorbing layer on an integrated structure type carrier and layering a hydrogen generating and nitrogen oxides cleaning catalyst layer, where hydrogen is generated from hydrocarbon and/or carbon monoxide contained in the exhaust gas and nitrogen oxides are cleaned by using the generated hydrogen, on the HC adsorbing layer.

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(71)出願人　000003997
日産自動車株式会社
神奈川県横浜市神奈川区宝町２番地

(72)発明者　山本　伸司
神奈川県横浜市神奈川区宝町２番地　日産自動車株式会社内

(74)代理人　100102141
弁理士　的場　基憲

最終頁に続く

(54)【発明の名称】　排気ガス浄化用触媒

(57)【要約】
【課題】　酸素過剰雰囲気下において、H_2を還元剤としてＮＯｘを高効率で浄化し、且つ、未浄化で排出されていたＨＣ、ＣＯ成分、特にエンジン始動後の低温域でのＨＣを著しく低減し、しかも燃費向上効果の高い排気ガス浄化用触媒を提供すること。
【解決手段】　一体構造型担体上にＨＣ吸着層を積層し、この上にH_2生成・ＮＯｘ浄化触媒層を積層して成る排気ガス浄化用触媒であって、ＨＣ吸着層がゼオライトを含有し、H_2生成・ＮＯｘ浄化触媒層が、炭化水素及び／又は一酸化炭素から水素を生成し、生成した水素を用いて窒素酸化物を浄化する。

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【特許請求の範囲】

【請求項１】　一体構造型担体上にＨＣ吸着層を積層し、この上にH_2生成・ＮＯｘ浄化触媒層を積層して成る排気ガス浄化用触媒であって、
上記H_2生成・ＮＯｘ浄化触媒層が、炭化水素及び／又は一酸化炭素から水素を生成し、生成した水素を用いて窒素酸化物を浄化することを特徴とする排気ガス浄化用触媒。

【請求項２】　上記H_2生成・ＮＯｘ浄化触媒層が、対象とする内燃機関のコールド運転時に上記ＨＣ吸着層に吸着し暖機運転過程で脱離する炭化水素と、内燃機関の暖機運転後に排出される炭化水素及び／又は一酸化炭素から水素を生成し、これら水素と排気ガス中の炭化炭素及び／又は一酸化炭素を用いて窒素酸化物を浄化することを特徴とする請求項１記載の排気ガス浄化用触媒。

【請求項３】　上記H_2生成・ＮＯｘ浄化触媒層がH_2生成触媒成分とＮＯｘ浄化触媒成分とを含み、
上記H_2生成触媒成分は、炭化水素を改質して水素を生成するＨＣ改質成分と、ＣＯを水蒸気改質して水素を生成するＣＯ改質成分とを含有し、
上記ＨＣ改質成分は、パラジウムを担持したセリウム酸化物を含有し、上記ＣＯ改質成分は、ロジウムを担持したジルコニウム酸化物を含有し、
上記H_2生成・ＮＯｘ浄化触媒層が、上記ＨＣ改質成分と上記ＣＯ改質成分とが混合されて同一層を形成すること、上記ＨＣ改質成分の上に上記ＣＯ改質成分が積層されること、又は排気ガスの流れ方向の上流側に上記ＨＣ改質成分が配置され且つ下流側に上記ＣＯ改質成分が配置されることのいずれかから構成されていることを特徴とする請求項１又は２記載の排気ガス浄化用触媒。

【請求項４】　上記H_2生成・ＮＯｘ浄化触媒層の触媒入口側部分が、パラジウムを担持したアルミナを含有する触媒層を含むことを特徴とする請求項１～３のいずれか１つの項に記載の排気ガス浄化用触媒。

【請求項５】　上記窒素酸化物を浄化するときの触媒入口の排気ガスが、水素量／全還元成分量≧０．３で表されるガス組成を満足することを特徴とする請求項１～４のいずれか１つの項に記載の排気ガス浄化用触媒。

【請求項６】　上記ロジウムを担持したジルコニウム酸化物が、アルカリ土類金属を含有し、その組成が次式①
［Ｘ］ａＺｒｂＯｃ…①
（式中のＸは、マグネシウム、カルシウム、ストロンチウム及びバリウムから成る群より選ばれた少なくとも１種の元素、ａ及びｂは、原子比率、ｃは、Ｘ及びＺｒの原子価を満足するのに必要な酸素原子数を示し、ａ＝０．０１～０．５、ｂ＝０．５～０．９９、ａ＋ｂ＝１を満たす）で表されることを特徴とする請求項３～５のいずれか１つの項に記載の排気ガス浄化用触媒。

【請求項７】　上記ＨＣ吸着層、上記ＨＣ改質成分を含有する触媒層、上記ＣＯ改質成分を含有する触媒層及び

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上記パラジウムを担持したアルミナを含有する触媒層から成る群より選ばれた少なくとも１つの触媒層が、ＮＯｘ浄化触媒成分を含有することを特徴とする請求項４～６のいずれか１つの項に記載の排気ガス浄化用触媒。

【請求項８】　上記ＨＣ吸着層、上記ＨＣ改質成分を含有する触媒層、上記ＣＯ改質成分を含有する触媒層及び上記パラジウムを担持したアルミナを含有する触媒層から成る群より選ばれた少なくとも１つの触媒層が、パラジウム、白金、ロジウム、アルミナ、アルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも１種のＮＯｘ還元成分を含有することを特徴とする請求項４～７のいずれか１つの項に記載の排気ガス浄化用触媒。

【請求項９】　上記アルカリ金属及び／又はアルカリ土類金属が、カリウム、セシウム、マグネシウム、カルシウム及びバリウムから成る群より選ばれた少なくとも１種の元素を含有することを特徴とする請求項８記載の排気ガス浄化用触媒。

【請求項１０】　上記ＨＣ吸着層が、Ｓｉ／２Ａｌ比＝１０～５００のＨ型β－ゼオライトを含有することを特徴とする請求項１～９のいずれか１つの項に記載の排気ガス浄化用触媒。

【請求項１１】　上記ＨＣ吸着層が、Ｈ型β－ゼオライトと、ＭＦＩ、Ｙ型、ＵＳＹ及びモルデナイトから成る群より選ばれた少なくとも１種のゼオライトとを含有することを特徴とする請求項１～１０のいずれか１つの項に記載の排気ガス浄化用触媒。

【請求項１２】　上記ＨＣ吸着層のゼオライトが、パラジウム、マグネシウム、カルシウム、ストロンチウム、バリウム、銀、イットリウム、ランタン、セリウム、ネオジム、リン、ホウ素及びジルコニウムから成る群より選ばれた少なくとも１種の元素を含有することを特徴とする請求項１０又は１１記載の排気ガス浄化用触媒。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、排ガス浄化用触媒に係り、更に詳細には、酸素過剰排ガス中の窒素酸化物（ＮＯｘ）を高効率で浄化する排気ガス浄化用触媒に関する。

【０００２】

【従来の技術】従来、自動車等の内燃機関の排気ガス浄化用触媒として、一酸化炭素（ＣＯ）及び炭化水素（ＨＣ）の酸化とＮＯｘの還元とを同時に行う触媒が汎用されている。このような触媒としては、耐火性担体上のアルミナコート層に、パラジウム（Ｐｄ）、白金（Ｐｔ）やロジウム（Ｒｈ）等の貴金属を担持させたもの及び必要に応じて助触媒成分としてセリウム（Ｃｅ）、ランタン（Ｌａ）等の希土類金属やニッケル（Ｎｉ）等のベースメタル酸化物を添加したもの等が開示されている（特開昭５８－２０３０７号公報）。上記公報に開示されて

いる触媒は、排ガス温度及びエンジンの設定空燃比の影響を強く受け、特に内燃機関の排ガスが酸素過剰のときには、ＮＯｘを浄化することができない。このような内燃機関の排ガスが酸素過剰の時に窒素酸化物を浄化する方法として、特許掲載２６００４２９号公報に、排ガスが酸素過剰のときにＮＯｘを吸蔵させ、その後酸素濃度を低下させて一時的にリッチ雰囲気にすることにより、吸蔵されたＮＯｘを放出して浄化処理する、いわゆるリッチスパイクによる方法が開示されている。

【０００３】

【発明が解決しようとする課題】しかしながら、上記公報で開示されているような、リッチスパイクによる方法では、酸素過剰の運転領域においても定期的に排ガス中の酸素濃度を低下させる必要があり、更に、酸素濃度が低下した条件下でＮＯｘを還元反応させるために、還元剤として多量のＨＣ、ＣＯを供給する必要があり、酸素過剰で走行することによる燃費向上の効果が十分に得られないという課題があった。

【０００４】更に、酸素過剰雰囲気においてＮＯｘを吸蔵させるために多量のアルカリ金属元素やアルカリ土類金属元素を含有させるが、このために活性金属であるＰｔ、Ｐｄ及びＲｈの低温時の酸化活性が十分に得られなくなる。また、ＮＯｘ浄化反応で消費されなかったＨＣ、ＣＯ成分を十分に浄化するためには、酸化反応で浄化させるか、ＮＯｘ浄化触媒の後段に三元触媒を配置して浄化する必要がある。しかしながら、このような触媒システムでは、ＨＣ、ＣＯを浄化する触媒が排気流路の後段に配置されるため、十分なＨＣ、ＣＯの浄化性能が得られず、特にエンジン始動直後に排出されるＨＣ、ＣＯ成分浄化が困難であるという課題もあった。

【０００５】本発明は、このような従来技術の有する課題に鑑みてなされたものであり、その目的とするところは、酸素過剰雰囲気下において、ＮＯｘを高効率で浄化し、且つ、未浄化で排出されていたＨＣ、ＣＯ成分、特にエンジン始動後の低温域でのＨＣを著しく低減し、しかも燃費向上効果の高い排気ガス浄化用触媒を提供することにある。

【０００６】

【課題を解決するための手段】本発明者は、上記課題を解決すべく、鋭意検討を行った結果、特定のＨＣ改質処理とＣＯ水蒸気改質処理等を行ってH_2を生成し、このH_2をＮＯｘ還元剤とすることにより、上記課題が解決できることを見出し、本発明を完成するに至った。

【０００７】即ち、本発明の排気ガス浄化用触媒は、一体構造型担体上にＨＣ吸着層を積層し、この上にH_2生成・ＮＯｘ浄化触媒層を積層して成る排気ガス浄化用触媒であって、上記H_2生成・ＮＯｘ浄化触媒層が、炭化水素及び／又は一酸化炭素から水素を生成し、生成した水素を用いて窒素酸化物を浄化することを特徴とする。

【０００８】また、本発明の排気ガス浄化用触媒の好適

形態は、上記H_2生成・ＮＯｘ浄化触媒層が、対象とする内燃機関のコールド運転時に上記ＨＣ吸着層に吸着し暖機運転過程で脱離する炭化水素と、内燃機関の暖機運転後に排出される炭化水素及び／又は一酸化炭素から水素を生成し、これら水素と排気ガス中の炭化炭素及び／又は一酸化炭素を用いて窒素酸化物を浄化することを特徴とする。

【０００９】更に、本発明の排気ガス浄化用触媒の他の好適形態は、上記H_2生成・ＮＯｘ浄化触媒層がH_2生成触媒成分とＮＯｘ浄化触媒成分とを含み、上記H_2生成触媒成分は、炭化水素を改質して水素を生成するＨＣ改質成分と、ＣＯを水蒸気改質して水素を生成するＣＯ改質成分とを含有し、上記ＨＣ改質成分は、パラジウムを担持したセリウム酸化物を含有し、上記ＣＯ改質成分は、ロジウムを担持したジルコニウム酸化物を含有し、上記H_2生成・ＮＯｘ浄化触媒層が、上記ＨＣ改質成分と上記ＣＯ改質成分とが混合されて同一層を形成すること、上記ＨＣ改質成分の上に上記ＣＯ改質成分が積層されること、又は排気ガスの流れ方向の上流側に上記ＨＣ改質成分が配置され且つ下流側に上記ＣＯ改質成分が配置されることのいずれかから構成されていることを特徴とする。

【００１０】更にまた、本発明の排気ガス浄化用触媒の他の好適形態は、上記H_2生成・ＮＯｘ浄化触媒層の触媒入口側部分が、パラジウムを担持したアルミナを含有する触媒層を含むことを特徴とする。

【００１１】また、本発明の排気ガス浄化用触媒の更に他の好適形態は、上記窒素酸化物を浄化するときの触媒入口の排気ガスが、水素量／全還元成分量≧０．３で表されるガス組成を満足することを特徴とする。

【００１２】更にまた、本発明の排気ガス浄化用触媒の他の好適形態は、上記ロジウムを担持したジルコニウム酸化物が、アルカリ土類金属を含有し、その組成が次式①

［Ｘ］ａＺｒｂＯｃ…①

（式中のＸは、マグネシウム、カルシウム、ストロンチウム及びバリウムから成る群より選ばれた少なくとも１種の元素、ａ及びｂは、原子比率、ｃは、Ｘ及びＺｒの原子価を満足するのに必要な酸素原子数を示し、ａ＝０．０１～０．５、ｂ＝０．５～０．９９、ａ＋ｂ＝１を満たす）で表されることを特徴とする。

【００１３】また、本発明の排気ガス浄化用触媒の他の好適形態は、上記ＨＣ吸着層、上記ＨＣ改質成分を含有する触媒層、上記ＣＯ改質成分を含有する触媒層及び上記パラジウムを担持したアルミナを含有する触媒層から成る群より選ばれた少なくとも１つの触媒層が、ＮＯｘ浄化触媒成分を含有することを特徴とする。

【００１４】更にまた、本発明の排気ガス浄化用触媒の他の好適形態は、上記ＨＣ吸着層、上記ＨＣ改質成分を含有する触媒層、上記ＣＯ改質成分を含有する触媒層及

び上記パラジウムを担持したアルミナを含有する触媒層から成る群より選ばれた少なくとも１つの触媒層が、パラジウム、白金、ロジウム、アルミナ、アルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも１種のＮＯｘ還元成分を含有することを特徴とする。

【００１５】また、本発明の排気ガス浄化用触媒の更に他の好適形態は、上記ＨＣ吸着層が、Ｓｉ／２Ａｌ比＝１０～５００のＨ型β－ゼオライトを含有することを特徴とする。

【００１６】更にまた、本発明の排気ガス浄化用触媒の他の好適形態は、上記ＨＣ吸着層が、Ｈ型β－ゼオライトと、ＭＦＩ、Ｙ型、ＵＳＹ及びモルデナイトから成る群より選ばれた少なくとも１種のゼオライトとを含有することを特徴とする。

【００１７】また、本発明の排気ガス浄化用触媒の他の好適形態は、上記ＨＣ吸着層のゼオライトが、パラジウム、マグネシウム、カルシウム、ストロンチウム、バリウム、銀、イットリウム、ランタン、セリウム、ネオジム、リン、ホウ素及びジルコニウムから成る群より選ばれた少なくとも１種の元素を含有することを特徴とする。

【００１８】

【発明の実施の形態】以下、本発明の排気ガス浄化用触媒について詳細に説明する。なお、「％」は特記しない限り、質量百分率を示す。本発明の排気ガス浄化用触媒は、一体構造型担体上に、ＨＣ吸着層を積層し、この上に、H_2生成・ＮＯｘ浄化触媒層を積層して成る。

【００１９】上記ＨＣ吸着層は、コールドＨＣ吸着能を持つゼオライトを主成分とし、対象とする内燃機関のコールド運転時、即ちエンジン始動直後で触媒がまだ低温であるときにはＨＣを吸着し、触媒暖機過程（１５０～３００℃）にあるときにはＨＣを脱離する。次に、上記ＨＣ吸着層に積層されているH_2生成・ＮＯｘ浄化触媒層は、後述するＨＣ・ＣＯ改質反応により、脱離ＨＣからH_2を生成し、更に、内燃機関の定常運転時に排出されるＨＣ及び／又はＣＯからもH_2を生成することができる。これらの生成されたH_2は、ＮＯｘ還元剤として排ガス中のＮＯｘとよく反応する。このとき、H_2生成・ＮＯｘ浄化触媒層に含まれるＮＯｘ浄化触媒成分は、温度が上昇しておらず十分に活性化してはいないが、H_2とＮＯｘとの反応性が高いため、エンジン始動直後から酸素過剰雰囲気の運転制御に到達するまでの触媒暖機過程中に排出されるＮＯｘを効率よく浄化することができると推察される。

【００２０】また、上記H_2生成・ＮＯｘ浄化触媒層で行われる上記ＨＣ・ＣＯ改質反応は、一般的には、ＨＣの改質反応とＣＯ水蒸気改質反応に分けることができ、このＨＣ改質反応は、次式②及び③

$$HC+O_2 \rightarrow HC(O)+CO+CO_2+H_2O+H_2 \cdots ②$$

$$HC+H_2O \rightarrow HC(O)+CO+CO_2+H_2 \cdots ③$$

（式中のＨＣ（Ｏ）は改質反応後のＨＣを示す）で表され、また上記ＣＯ水蒸気改質反応は、次式④

$$CO+H_2O \rightarrow CO_2+H_2 \cdots ④$$

で表されると考えられている。

【００２１】上記ＨＣ・ＣＯ改質反応によりH_2を生成させるに際し、上記H_2生成・ＮＯｘ浄化触媒層は、上記ＨＣ吸着層上に積層される。この層は、ＨＣを改質してH_2を生成するＨＣ改質成分とＣＯを水蒸気改質してH_2を生成するＣＯ改質成分とが混合されて一つの層を形成し、又はＨＣ改質成分を含むＨＣ改質成分層と、ＣＯ改質成分を含むＣＯ水蒸気改質層とが積層されている多層を形成するが、特に、ＨＣ改質成分層の上にＣＯ水蒸気改質成分層を積層した構造を採ることが好ましい。図１に示したように、エンジン始動直後に上記ＨＣ吸着層に吸着され、触媒暖機過程で上記ＨＣ吸着層から放出されたＨＣは、まず、上記ＨＣ改質成分層で部分酸化物、ＨＣ（Ｏ）、ＣＯ及びH_2に改質され、更に上記ＣＯ水蒸気改質成分層でＣＯがH_2に変成される。このような構造を採ることにより、上述の如く触媒暖機過程中においても、排気ガス中に含まれるＨＣ及びＣＯを改質しH_2を生成できるので、酸素過剰運転領域においても、H_2を供給し、触媒暖機後もＮＯｘを浄化処理できる。なお、ＨＣがＨＣ改質反応、ＣＯ水蒸気改質反応の順で変成されればよいので、上記ＨＣ改質成分層と上記ＣＯ水蒸気改質成分層が排気ガス流路に沿ってタンデム配置を採ってもよく、上記多層構造に特に限定されるものではない。

【００２２】

更に、ＨＣを改質しH_2を生成するためには、上記ＨＣ改質成分層にＰｄを担持したセリウム酸化物を含有させることが好ましく、ＣＯを水蒸気改質してH_2を生成するためには、上記ＣＯ水蒸気改質成分層にＲｈを担持したジルコニウム酸化物を含有させることが好ましい。これらの貴金属や酸化物を含有させることにより、排ガスを本発明の排ガス浄化用触媒内に通過させた場合、上記ＨＣ改質成分層においては、主に次式③～⑤

$$HC+O_2 \rightarrow HC(O)+CO+CO_2+H_2 \cdots ⑤$$

$$HC+H_2O \rightarrow HC(O)+CO+CO_2+H_2 \cdots ③$$

$$CO+H_2O \rightarrow CO_2+H_2 \cdots ④$$

の反応が起こり、上記ＣＯ水蒸気改質成分層においては、主に次式③、④及び⑥

$$CO+H_2O \rightarrow CO_2+H_2 \cdots ④$$

$$HC+H_2O \rightarrow HC(O)+CO+CO_2+H_2 \cdots ③$$

$HC(O)+H_2O \rightarrow HC(O)'+CO_2+CO+H_2$…⑥

の反応が起こり、H_2が生成されるとともに排ガス成分、特にＨＣとＣＯが浄化される。

【００２３】更にまた、上記H_2生成・ＮＯｘ浄化触媒層が上述のようなH_2生成触媒成分だけではなく、ＮＯｘ浄化触媒成分をも含むことにより、１つの触媒でＮＯｘ還元剤であるH_2を生成するとともに、ＮＯｘを効率よく浄化することができる。

【００２４】更に、エンジン暖機過程終了後においても、排ガス中のＨＣ、ＣＯからH_2を有意に生成させるために、本発明の排気ガス浄化用触媒は、上流側の上記H_2生成触媒の一部、即ち該触媒入口側部分が、Ｐｄを担持したアルミナを含有する触媒層を含むことが好ましい。例えば、本発明の排気ガス浄化用触媒の好適な一形態として、触媒入口側には上記ＨＣ吸着触媒層の上にＰｄ担持アルミナを含有するＨＣ部分酸化触媒が積層されており、その下流側には上記ＨＣ吸着層の上にＰｄ担持セリウム酸化物を含有するＨＣ改質成分層とＲｈ担持ジルコニウム酸化物を含有するＣＯ水蒸気改質成分層とが積層されている構造が挙げられる。図２に、上記構造を示すが、本発明の排ガス浄化用触媒は特にこれに限定されるものではない。

【００２５】また、図２に示したように、触媒暖機後においては、上記該触媒入口側部分に配置したＰｄを担持したアルミナを含有する触媒層で、部分酸化反応により排気ガス中に含まれるＨＣがＨＣ（Ｏ）・ＣＯに変成され、次に、上記ＨＣ改質成分層でＨＣ（Ｏ）の改質反応によりH_2生成が促進され、次いで上記ＣＯ水蒸気改質成分層で水蒸気改質反応によりＣＯとH_2OからCO_2とH_2が生成されていると推察される。従って、本発明においては、上述の触媒暖機過程に引き続いて、触媒暖機後もH_2を供給でき、酸素過剰雰囲気下であってもＮＯｘを還元浄化できると考えられる。

【００２６】このように、本発明の排気ガス浄化用触媒においては、ＮＯｘ浄化に用いる還元成分として、従来から主として用いられていたＨＣ及びＣＯの代わりに又はこれに加えてH_2を用いるこができるが、更に、ＮＯｘ浄化するときの触媒入口の排気ガスは、H_2量／全還元成分量≧０．３で表されるガス組成を満足することが好ましい。かかるガス組成を満足すれば、排気ガス中のH_2濃度が高くなるので、更に高いＮＯｘ浄化性能を得ることができる。

【００２７】即ち、従来、自動車エンジンからの排気ガスや排ガス触媒を用いた場合の排ガス中のH_2比率はH_2量／全還元成分量＜０．３であり、H_2の比率が低く、H_2を還元成分として有効利用することが不可能であったが、本発明ではこの比率を増大し、H_2を有効利用しているのである。なお、上記排ガス組成は、H_2量／全還元成分量≧０．３を満足すれば十分であるが、H_2量／全還元成分量≧０．５とすることが更に好ましい。

【００２８】また、上記ＣＯ水蒸気改質成分層において、上記Ｒｈの酸化状態をＣＯ水蒸気改質反応に適した状態に維持するために、上記Ｒｈ担持ジルコニウム酸化物がアルカリ土類金属を含有して成ることが好ましく、その組成は、次式①

［Ｘ］ａＺｒｂＯｃ…①

で表される。上記式①のＸは、Ｍｇ、Ｃａ、Ｓｒ又はＢａ及びこれらの任意の組み合わせに係る元素を示し、ａは、該元素の原子比率、ｂは、Ｚｒの原子比率、ｃは、該元素及びＺｒの原子価を満足するのに必要な酸素原子数を示し、また、ａ＝０．０１～０．５、ｂ＝０．５～０．９９、ａ＋ｂ＝１を満たす。上記アルカリ土類金属を含有させれば、初期から耐久後まで高い触媒活性を得ることができる。

【００２９】更に、上記ＨＣ吸着層、上記H_2生成・ＮＯｘ浄化触媒層又は上記Ｐｄを担持したアルミナを含有する触媒層及びこれらの任意の組み合わせに係る触媒層は、ＮＯｘ浄化触媒成分を含有することが好ましい。即ち、上記ＨＣ吸着層、ＨＣ改質成分層、ＣＯ水蒸気改質成分層及び該触媒入口側部分に配置されたＰｄを担持したアルミナを含有する触媒層のいずれにもＮＯｘ浄化触媒成分であるＰｄ、ＰｔやＲｈ等を含有させることができる。ＮＯｘ浄化触媒成分を含有させることによって、触媒暖機過程でH_2を生成させると同時に、触媒暖機過程で排出されるＮＯｘを効率よく浄化することができ、更には、触媒暖機後も酸素過剰雰囲気下での運転制御時に排出されるＮＯｘを効率よく浄化することができる。なお、上述のように各触媒層にＮＯｘ浄化触媒成分を含有させるだけでなく、上記H_2生成・ＮＯｘ浄化触媒層の上に更にＮＯｘ浄化触媒層を積層してもよいし、各触媒層にＮＯｘ浄化触媒成分を含有させずにＮＯｘ浄化触媒層を積層してもよい。更には、排ガス流路上流側に本発明の排ガス浄化用触媒を、下流側にＮＯｘ浄化用触媒をタンデム配置してもかまわない。

【００３０】また特に、上記ＨＣ吸着層、ＨＣ改質成分層、ＣＯ水蒸気改質成分層又は上記触媒入口側部分に配置されているＰｄを担持したアルミナを含有する触媒層及びこれらの任意の組み合わせに係る触媒層は、Ｐｄ、Ｐｔ、Ｒｈ、アルミナ、アルカリ金属又はアルカリ土類金属及びこれらの任意の組み合わせに係るＮＯｘ浄化触媒成分を含有することができる。これらのＮＯｘ浄化成分を含有することによって、エンジン始動直後から酸素過剰雰囲気の定常運転制御時まで、エンジンから排出されるＮＯｘを効率よく浄化できる。なお、上記アルカリ金属及び／又はアルカリ土類金属としては、カリウム（Ｋ）、セシウム（Ｃｅ）、マグネシウム（Ｍｇ）、カルシウム（Ｃａ）又はバリウム（Ｂａ）及びこれらの任意の組み合せに係る金属を挙げることができるが、これ

らに限定されるものではない。

【００３１】更に、上記各触媒層全体における上記アルカリ金属及びアルカリ土類金属含有量が、本発明の排ガス浄化用触媒における該金属含有総量の８０重量%以上になると、コールドリーン域において排出されるＮＯｘを吸収できるが、８０重量%未満になると、十分なＮＯｘ吸収能が得られない。また、上記各触媒層全体がアルカリ金属及びアルカリ土類金属の総量の８０重量%以上を含有するためには、アルカリ金属及び／又はアルカリ土類金属が、不溶性の化合物及び／又は難溶性の化合物であることが好ましい。

【００３２】また、上記ＨＣ吸着層で使用するゼオライトは、公知のゼオライトの中から適宜選択して使用することができるが、特に、常温から比較的高い温度で、しかも、水存在雰囲気下であっても十分なＨＣ吸着能を有し、且つ、高い耐久性を有するものを選択することが好ましい。このようなゼオライトとしては、代表的に、Ｓｉ／２Ａｌ比が１０～５００のH型β－ゼオライトが挙げられるが、特にこれに限定されるものではない。Ｓｉ／２Ａｌ比が１０未満のゼオライトでは、排ガス中に共存する水分の吸着阻害が大きいため、有効にＨＣを吸着することができず、Ｓｉ／２Ａｌ比が５００を超えるゼオライトでは、ＨＣ吸着能が低下してしまうことがある。

【００３３】更に、エンジンから排出される排ガス成分に合わせて、細孔径や細孔構造の異なるＭＦＩ、Ｙ型、ＵＳＹ又はモルデナイト及びこれらの任意の組み合わせに係るゼオライトを選択して、上記H型β－ゼオライトに混合して用いれば、排ガス中のＨＣを効率よく吸着することができる。

【００３４】なお、上記H型β－ゼオライトでも十分なＨＣ吸着能を有するが、上記各種ゼオライトに、Ｐｄ、Ｍｇ、Ｃａ、ストロンチウム（Ｓｒ）、Ｂａ、銀（Ａｇ）、イットリウム（Ｙ）、Ｌａ、Ｃｅ、ネオジム（Ｎｄ）、リン（Ｐ）、ホウ素（Ｂ）又はジルコニウム（Ｚｒ）及びこれらの任意の組み合わせに係る元素を、イオン交換法、含浸法及び浸漬法等の通常の方法を用いて担持することにより、ＨＣ吸着性能やＨＣ脱離抑制能を更に向上することができる。

【００３５】また、本発明の排気ガス浄化用触媒の上記一体構造型触媒担体には、例えばハニカム担体があり、ハニカム材料としては、一般にセラミック等のコージェライト質のものが多く用いられる。しかし、これに限られず、フェライト系ステンレス等の金属材料から成るハニカム材料を用いてもよく、更には触媒成分粉末そのものをハニカム形状に成形してもよい。

【００３６】

【実施例】以下、本発明を実施例及び比較例により更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【００３７】［ＨＣ改質成分層の触媒粉末の調製］硝酸Ｐｄ水溶液をセリウム酸化物（CeO_2）粉末に含浸し、乾燥・焼成してＰｄ担持セリウム酸化物粉末Ａを得た。この粉末のＰｄ担持濃度は１０％であった。また、CeO_2の代わりに、$Zr_{0.1}Ce_{0.9}O_2$とした以外は、粉末Ａと同様の操作を繰り返して得た粉末を、粉末Ｂとし、$Zr_{0.2}Ce_{0.8}O_2$としたものを粉末Ｃ、$Zr_{0.5}Ce_{0.5}O_2$としたものを粉末Ｄ、$Zr_{0.9}Ce_{0.1}O_2$としたものを粉末Ｅとした。更に、Ｐｄ担持濃度を５％とした以外は、粉末Ａと同様の操作を繰り返して得た粉末を粉末Ｆとした。

【００３８】［ＣＯ水蒸気改質成分層の触媒粉末の調製］硝酸Ｒｈ水溶液を$Ca_{0.2}Zr_{0.8}O_2$粉末に含浸し、乾燥・焼成してＲｈ担持ジルコニウム酸化物粉末Ｇを得た。この粉末のＲｈ担持濃度は６％であった。また、$Ca_{0.2}Zr_{0.8}O_2$の代わりに、$Mg_{0.1}Zr_{0.9}O_2$とした以外は、粉末Ｇと同様の操作を繰り返して得た粉末を粉末Hとし、$Ba_{0.1}Zr_{0.9}O_2$としたものを粉末Ｉ、$Sr_{0.2}Zr_{0.8}O_2$としたものを粉末Ｊ、$Ca_{0.1}Mg_{0.1}Zr_{0.8}O_2$としたものを粉末K、$Ca_{0.1}Ba_{0.05}Mg_{0.05}Zr_{0.8}O_2$としたものを粉末Ｌ、$Ca_{0.01}Zr_{0.99}O_2$としたものを粉末Ｍ、$Ca_{0.5}Zr_{0.5}O_2$としたものを粉末Nとした。

【００３９】［Ｐｄを担持したアルミナを含有する触媒層の触媒粉末の調製］硝酸Ｐｄ水溶液を活性アルミナ（Al_2O_3）粉末に含浸し、乾燥・焼成してＰｄ担持アルミナ粉末Oを得た。この粉末のＰｄ担持濃度は１５％であった。また、Al_2O_3の代わりに、Ｃｅを３％含有するAl_2O_3とした以外は、粉末Oと同様の操作を繰り返して得た粉末を粉末Ｐとし、Ｚｒを３％含有するAl_2O_3としたものを粉末Q、Ｌａを３%含有するAl_2O_3としたものを粉末R、Ｚｒを１０%含有するAl_2O_3としたものを粉末Ｓとした。

【００４０】［ＮＯｘ浄化触媒成分を含有する触媒粉末の調製］硝酸Ｐｄ水溶液を、Al_2O_3粉末に含浸し、乾燥・焼成してＰｄ担持アルミナ粉末Ｔを得た。この粉末ＴのＰｄ担持濃度は８％であった。ジニトロジアンミンＰｔ酸水溶液を、Al_2O_3粉末に含浸し、乾燥・焼成してＰｔ担持アルミナ粉末Uを得た。この粉末UのＰｔ担持濃度は６％であった。硝酸Ｒｈ水溶液を、Al_2O_3粉末に含浸し、乾燥・焼成してＲｈ担持アルミナ粉末Vを得た。この粉末VのＲｈ担持濃度は４％であった。

【００４１】［触媒調製１］β－ゼオライト（Ｓｉ／２Ａｌ＝２５）９００ｇとシリカゾル１００ｇと純水１０００ｇを混合粉砕してスラリーとし、コージェライト質モノリス担体（９００セル／４ミル、１．３L）に付着させ、乾燥・焼成したのち、ゼオライトコート量１００

ｇ／Ｌのゼオライト触媒を得た。次いで、粉末Ａ７０６ｇと硝酸性アルミナバインダー１２ｇと純水８００ｇとを混合粉砕してスラリーとし、ゼオライト触媒に付着させ、乾燥・焼成し、ゼオライト触媒に７２ｇ／Ｌをコートした触媒Ａを得た。この触媒ＡのＰｄ担持量は、７．０６ｇ．／Ｌであった。更に、粉末Ｇ５８８ｇと硝酸性アルミナバインダー１２ｇと純水６００ｇとを混合粉砕してスラリーとし、触媒Ａに付着させ、乾燥・焼成し、触媒Ａに６０ｇ／Ｌをコートした触媒ＡＧ１を得た。この触媒ＡＧ１のＲｈ担持量は、３．５３ｇ／Ｌであった。触媒ＡＧ１は、図３に示す三層構造とした。また、β－ゼオライト（Ｓｉ／２Ａｌ＝２５）の代わりに表２に示したＨＣ吸着材を用いて、同様の操作を繰り返し、触媒ＡＧ２～７を得た。

【００４２】［触媒調製２］粉末Ｂ７０６ｇと硝酸性アルミナバインダー１４ｇと純水８００ｇを混合粉砕してスラリーとし、触媒調整１と同様の操作を繰り返して調製したゼオライト触媒に付着させ、乾燥・焼成し、ゼオライト触媒に７２ｇ／Ｌをコートした触媒Ｂを得た。この触媒ＢのＰｄ担持量は、７．０６ｇ／Ｌであった。次に、粉末Ｇ５８８ｇと硝酸性アルミナバインダー１２ｇと純水６００ｇを混合粉砕してスラリーとし、触媒Ｂに付着させ、乾燥・焼成し、触媒Ｂに６０ｇ／Ｌをコートした触媒ＢＧを得た。この触媒ＢＧのＲｈ担持量は、３．５３ｇ／Ｌであった。触媒ＢＧは、図３に示す三層構造とした。また、粉末Ｂの代わりに粉末Ｃ～Ｆを用いて、同様の操作を繰り返して、触媒ＣＧ、ＤＧ、ＥＧ、ＦＧを得た。

【００４３】［触媒調製３］β－ゼオライト（Ｓｉ／２Ａｌ＝２５）の代わりに表２に示したＨＣ吸着材とした以外は、触媒調整１と同様の操作を繰り返し、ゼオライト触媒を得た。次に、粉末Ｂ７０６ｇと粉末Ａ７０６ｇと硝酸性アルミナバインダー２８ｇと純水１５００ｇを混合粉砕してスラリーとし、ゼオライト触媒に付着させ、乾燥・焼成し、ゼオライト触媒に１４４ｇ／Ｌをコートした触媒ＢＡを得た。この触媒ＢＡのＰｄ担持量は、１４．１２ｇ／Ｌであった。更に、粉末Ｈ５８８ｇと硝酸性アルミナバインダー１２ｇと純水６００ｇとを混合粉砕してスラリーとし、触媒ＢＡに付着させ、乾燥・焼成し、触媒ＢＡに６０ｇ／Ｌをコートした触媒ＢＡＨを得た。この触媒ＢＡＨのＲｈ担持量は、３．５３ｇ／Ｌであった。触媒ＢＡＨは、図３に示す三層構造とした。また、粉末Ｈの代わりに粉末Ｉ～Ｎを用いて、同様の操作を繰り返して、触媒ＢＡＩ、ＢＡＪ、ＢＡＫ、ＢＡＬ、ＢＡＭ、ＢＡＮを得た。

【００４４】［触媒調製４］β－ゼオライト（Ｓｉ／２Ａｌ＝２５）９００ｇとシリカゾル１００ｇと純水１０００ｇを混合粉砕してスラリーとし、コージェライト質モノリス担体（９００セル／４ミル、１．３Ｌ）に付着させ、乾燥・焼成したのち、ゼオライトコート量５０ｇ／Ｌのゼオライト触媒を得た。これに、粉末Ｏ４７１ｇと硝酸性アルミナバインダー９ｇと純水５００ｇとを混合粉砕してスラリーとし、ゼオライト触媒の排気ガス入口側の１／４部分に付着させ、乾燥・焼成し、ゼオライト触媒に４８ｇ／Ｌをコートした触媒Ｏ１を得た。この触媒Ｏ１のＰｄ担持量は、７．０６ｇ／Ｌであった。次いで、粉末Ｂ７０６ｇと粉末Ａ７０６ｇと硝酸性アルミナバインダー２８ｇと純水１０００ｇとを混合粉砕してスラリーとし、触媒Ｏ１をコートしていない３／４部分に付着させ、乾燥・焼成し、１４４ｇ／Ｌをコートした触媒ＯＢＡを得た。この触媒ＯＢＡの総Ｐｄ担持量は、２１．１８ｇ／Ｌであった。更に、粉末Ｌ５８８ｇと硝酸性アルミナバインダー１２ｇと純水６００ｇとを混合粉砕してスラリーとし、触媒Ｏ１をコートしていない３／４部分に付着させ、乾燥・焼成し、触媒ＯＢＡに６０ｇ／Ｌをコートした触媒ＯＢＡＬを得た。この触媒ＯＢＡＬのＲｈ担持量は、３．５３ｇ／Ｌであった。触媒ＯＢＡＬは、図４に示す構造とした。また、β－ゼオライト（Ｓｉ／２Ａｌ＝２５）の代わりに表２に示すＨＣ吸着材を用いてゼオライトコート量５０ｇ／Ｌのゼオライト触媒を作成し、粉末Ｏの代わりに粉末Ｐ～Ｓを、粉末Ａの代わりに粉末Ｂ～Ｆを、粉末Ｌの代わりに粉末Ｇ～Ｋを用いて、同様の操作を繰り返して、触媒ＰＢＢＫ、ＱＢＣＪ、ＲＢＤＩ、ＳＢＥＨ、ＯＢＦＧを得た。

【００４５】［触媒調製５］粉末Ｂ７０６ｇと硝酸性アルミナバインダー１４ｇと純水１０００ｇとを混合粉砕してスラリーとし、触媒調製４と同様の操作を繰り返して得たゼオライト触媒に付着させ、乾燥・焼成し、７２ｇ／Ｌをコートした触媒Ｂ２を得た。この触媒Ｂ２のＰｄ担持量は、７．０６ｇ／Ｌであった。次いで、粉末Ｇ５８８ｇと硝酸性アルミナバインダー１２ｇと純水６００ｇとを混合粉砕してスラリーとし、触媒Ｂ２に付着させ、乾燥・焼成し、触媒Ｂ２に６０ｇ／Ｌをコートした触媒ＢＧを得た。この触媒ＢＧのＲｈ担持量は、３．５３ｇ／Ｌであった。更に、粉末Ｔ６１８ｇと、粉末Ｕ５３０ｇと、粉末Ｖ８８ｇと、水酸化ナトリウムをNa_2O換算で２０ｇと、酢酸バリウムをＢａＯ換算で２０ｇと、硝酸性アルミナバインダー１４ｇと、純水１５００ｇとを混合粉砕してスラリーとし、触媒ＢＧに付着させ、乾燥・焼成し、触媒ＢＧに１４７ｇ／Ｌをコートした触媒ＢＧＮ１を得た。この触媒BGN_1のＰｄ担持量は１２．０ｇ／Ｌ、Ｐｔ担持量は３．１８ｇ／Ｌ、Ｒｈ担持量は、３．８８ｇ／Ｌであった。触媒ＢＧＮ１は、図５に示す構造とした。

【００４６】［ＮＯｘ浄化用触媒の調製］粉末Ｔ６１８ｇと、粉末Ｕ５３０ｇと、粉末Ｖ８８ｇと、水酸化ナトリウムをＮａ２Ｏ換算で２０ｇと、酢酸バリウムをＢａＯ換算で２０ｇと、硝酸性アルミナバインダー１４ｇと、純水１５００ｇとを混合粉砕してスラリーとし、コージェライト質モノリス担体（４００セル／６ミル、

１．３Ｌ）に付着させ、乾燥・焼成し、１４７ｇ／Ｌをコートした触媒Ｎ１を得た。この触媒Ｎ１のＰｄ担持量は4．９４ｇ／Ｌ、Ｐｔ担持量は3．１８ｇ／Ｌ、Ｒｈ担持量は、０．３５ｇ／Ｌであった。触媒Ｎ１は、単層構造とした。また、水酸化ナトリウムの代わりに酢酸マグネシウムを用い、同様の操作を繰り返して、ＭｇＯとして１０ｇ／Ｌ、ＢａＯとして１０ｇ／Ｌを担持した触媒を触媒Ｎ２を得た。

【００４７】［三元触媒の調製］粉末Ｔ５６５ｇと、粉末Ｆ２２６ｇと、酢酸バリウムをＢａＯ換算で１０ｇと、硝酸性アルミナバインダー９ｇと、純水１０００ｇとを混合粉砕してスラリーとし、コージェライト質モノリス担体（９００セル／２ミル、１．３Ｌ）に付着させ、乾燥・焼成し、９０ｇ／Ｌをコートした触媒Ｔ０を得た。更に、粉末Ｖ１２８ｇと、$Ce_{0.2}Zr_{0.8}O_2$粉末２００ｇと、硝酸性アルミナバインダー１２ｇと、純水５００ｇとを混合粉砕してスラリーとし、触媒Ｔ０に付着させ、乾燥・焼成し、触媒Ｔ０に３４ｇ／Ｌをコートした二層構造の触媒Ｔ１を得た。この触媒Ｔ１のＰｄ担持量は5．６５ｇ／Ｌ、Ｒｈ担持量は、０．５１ｇ／Ｌであった。

【００４８】［触媒仕様］表１に、上記各触媒粉末の主な触媒成分等を示し、また表２に、上記各触媒調製により作成した触媒の仕様を示した。

【００４９】

【表１】

触媒粉末	担持貴金属種（－）	担持濃度（%）	担持基材
A	Pd	10.0	CeO_2
B	Pd	10.0	$Zr_{0.1}Ce_{0.9}O_2$
C	Pd	10.0	$Zr_{0.2}Ce_{0.8}O_2$
D	Pd	10.0	$Zr_{0.5}Ce_{0.5}O_2$
E	Pd	10.0	$Zr_{0.9}Ce_{0.1}O_2$
F	Pd	5.0	CeO_2
G	Rh	6.0	$Ca_{0.2}Zr_{0.8}O_2$
H	Rh	6.0	$Mg_{0.1}Zr_{0.9}O_2$
I	Rh	6.0	$Ba_{0.1}Zr_{0.9}O_2$
J	Rh	6.0	$Sr_{0.2}Zr_{0.8}O_2$
K	Rh	6.0	$Ca_{0.1}Mg_{0.1}Zr_{0.8}O_2$
L	Rh	6.0	$Ca_{0.1}Ba_{0.05}Mg_{0.05}Zr_{0.8}O_2$
M	Rh	6.0	$Ca_{0.01}Zr_{0.99}O_2$
N	Rh	6.0	$Ca_{0.5}Zr_{0.5}O_2$
O	Pd	15.0	Al_2O_3
P	Pd	15.0	Ce3%-Al_2O_3
Q	Pd	15.0	Zr3%-Al_2O_3
R	Pd	15.0	La3%-Al_2O_3
S	Pd	15.0	Zr10%-Al_2O_3
T	Pd	8.0	Al_2O_3
U	Pt	6.0	Al_2O_3
V	Rh	4.0	Al_2O_3

【００５０】

【表２】

触媒	触媒構造	貴金属担持量(g/L) Pd	Pt	Rh	(g/L) アルカリ	(g/L) アルカリ土類	HC吸着材層	第一層	第二層	第三層
AG1	図3	7.06	−	3.53	−	−	β(Si/2Al=25)	A	G	−
AG2	図3	7.06	−	3.53	−	−	β(Si/2Al=15)	A	G	−
AG3	図3	7.06	−	3.53	−	−	β(Si/2Al=300)	A	G	−
AG4	図3	7.06	−	3.53	−	−	β(=25)+ZSM5(30)	A	G	−
AG5	図3	7.06	−	3.53	−	−	β(=25)+USY(=15)	A	G	−
AG6	図3	7.06	−	3.53	−	−	Ag,P−β(=25)	A	G	−
AG7	図3	7.06	−	3.53	−	−	Pd−β(=25)	A	G	−
BG	図3	7.06	−	3.53	−	−	β(=25)	B	G	−
CG	図3	7.06	−	3.53	−	−	β(=25)	C	G	−
DG	図3	7.06	−	3.53	−	−	β(=25)	D	G	−
EG	図3	7.06	−	3.53	−	−	β(=25)	E	G	−
FG	図3	7.06	−	3.53	−	−	β(=25)	F	G	−
BAH	図3	14.12	−	3.53	−	−	β(=25)	B+A	H	−
BAI	図3	14.12	−	3.53	−	−	β(=25)	B+A	I	−
BAJ	図3	14.12	−	3.53	−	−	β(=25)	B+A	J	−
BAK	図3	14.12	−	3.53	−	−	β+ZSM5	B+A	K	−
BAL	図3	14.12	−	3.53	−	−	β+USY	B+A	L	−
BAM	図3	14.12	−	3.53	−	−	Ag,P−β	B+A	M	−
BAN	図3	14.12	−	3.53	−	−	Pd−β	B+A	N	−
OBAL	図4	21.18	−	3.53	−	−	β	O	B+A	L
PBBK	図4	21.18	−	3.53	−	−	β	P	2×B	K
QBCJ	図4	21.18	−	3.53	−	−	β+ZSM5	Q	B+C	J
RBDI	図4	21.18	−	3.53	−	−	β+USY	R	B+D	I
SBEH	図4	21.18	−	3.53	−	−	Ag,P−β	S	B+E	H
OBFG	図4	21.18	−	3.53	−	−	Pd−β	O	B+F	G
BGN1	図5	12.0	3.18	3.88	$(Na_2O)_2$	$(BaO)_{20}$	β	B	G	T+U+V
N1	単一層	4.94	3.18	0.35	$(Na_2O)_2$	$(BaO)_{20}$				
N2	単一層	4.94	3.18	0.35	$(MgO)_{10}$	$(BaO)_{10}$				
T1	単一層	5.85	−	0.51	−	$(BaO)_{10}$				

【００５１】＜各触媒の性能評価＞性能評価は車両評価を行い、北米でのテストモードであるＦＴＰ－７５モード（ＬＡ－４）にて走行した時の各排気ガス成分の排出量の測定を行った。本性能評価に用いた排気ガス浄化システムの構成を図６に示す。該システムは、触媒１及び２、エンジン１０、燃料噴射装置１１、O_2センサー１＊２、ＥＣＵ１３から成る。車両には排ガス流路上流側の触媒１に表３に示した触媒を配置し、その下流側の触媒２に上記ＮＯｘ浄化用触媒であるＮ１又はＮ２を配置し、実施例１～３０及び比較例１とした。排気ガスを上記システムにより浄化し、ＨＣ、ＣＯ及びＮＯｘの残存率を次式⑦

残存率＝｛１－（ＮＯｘ浄化触媒出口の排出ガス中のＨＣ、ＣＯ、ＮＯｘ排出量）／（エンジンアウトの排出ガス中のＨＣ、ＣＯ、ＮＯｘ排出量）｝×１００（％）…⑦

（上記排出ガス中のＨＣ、ＣＯ、ＮＯｘ排出量は、上記の車両評価モードを走行したときの排出量を示す）で表される計算式で調べた。また、表３は、上記の車両評価モードで走行する場合のスタート直後の走行部分、具体的にはＦＴＰ－７５モードのスタート後、約２００秒までの走行部分を除いた部分のＮＯｘ、ＨＣの各成分の平均濃度を用いて計算した値である。また、ＨＣ濃度も同様にして平均濃度を用いて計算した。スタート直後の走行部分を除いたのは、エンジンスタート直後に未燃焼のＨＣが排出され、ＨＣ濃度が高くなってしまい、正しく評価できないからである。なお、性能評価は、以下に示す条件で行った。

【００５２】

（耐久条件）

エンジン排気量　３０００ｃｃ

燃料　日石ダッシュガソリン　（Ｐｂ＝０ｍｇ／ｕｓｇ、Ｓ＝３０ｐｐｍ以下）

触媒入口ガス温度　６５０℃

耐久時間　５０時間

【００５３】

（性能評価条件）

触媒容量　触媒１：本発明の触媒　１．３Ｌ
触媒２：ＮＯｘ浄化触媒　１．３Ｌ

評価車両　日産自動車株式会社製　直噴１．８Ｌエンジン

【００５４】得られた結果を表３に示した。

【００５５】

【表３】

	搭載位置		残存率（%）		
	1 触媒	2 触媒	HC	CO	NOx
実施例1	AG1	N1	1.3	1.9	2.4
実施例2	AG2	N1	1.2	1.8	2.2
実施例3	AG3	N1	1.1	1.7	2.1
実施例4	AG4	N1	1.1	1.8	1.9
実施例5	AG5	N1	1.2	1.8	2.0
実施例6	AG6	N1	1.2	1.7	2.0
実施例7	AG7	N1	1.2	1.8	2.1
実施例8	BG	N1	1.2	1.7	1.9
実施例9	CG	N1	1.3	1.6	2.1
実施例10	DG	N1	1.3	1.6	2.2
実施例11	EG	N1	1.2	1.7	2.0
実施例12	FG	N1	1.2	1.8	2.1
実施例13	BAH	N1	1.1	1.9	1.9
実施例14	BAI	N1	1.1	1.8	1.9
実施例15	BAJ	N1	1.1	1.8	2.0
実施例16	BAK	N1	1.2	1.8	2.0
実施例17	BAL	N1	1.1	1.9	2.1
実施例18	BAM	N1	1.2	1.8	2.1
実施例19	BAN	N1	1.3	1.8	2.2
実施例20	OBAL	N1	1.4	2.0	2.2
実施例21	PBBK	N1	1.2	1.8	2.1
実施例22	QBCJ	N1	1.1	1.9	1.9
実施例23	RBDI	N1	1.1	1.8	1.9
実施例24	SBEH	N1	1.1	1.8	2.0
実施例25	OBFG	N1	1.2	1.8	2.0
実施例26	BGN1	N1	1.3	2.4	2.2
実施例27	AG1	N2	1.2	1.7	2.0
実施例28	BG1	N2	1.3	1.6	2.1
実施例29	BAH	N2	1.2	1.7	2.1
実施例30	OBFG	N2	1.1	1.8	2.0
比較例1	T1	N1	4.2	7.1	7.3

【００５６】

【発明の効果】以上、説明したように、本発明によれば、特定のＨＣ改質処理とＣＯ水蒸気改質処理等を行ってH_2を生成し、このH_2をＮＯｘ還元剤とすることに

より、酸素過剰雰囲気下において、H_2を還元剤としてＮＯｘを高効率で浄化し、且つ、未浄化で排出されていたＨＣ、ＣＯ成分、特にエンジン始動後の低温域でのＨＣを著しく低減し、しかも燃費向上効果の高い排気ガス浄化用触媒を提供することができる。

【図面の簡単な説明】

【図１】本発明の排気ガス浄化用触媒の一例を示す横断面図である。

【図２】本発明の排気ガス浄化用触媒の他の例を示す縦断面図である。

【図３】本発明の排気ガス浄化用触媒の他の例を示す縦断面図である。

【図４】本発明の排気ガス浄化用触媒の他の例を示す縦＊断面図である。

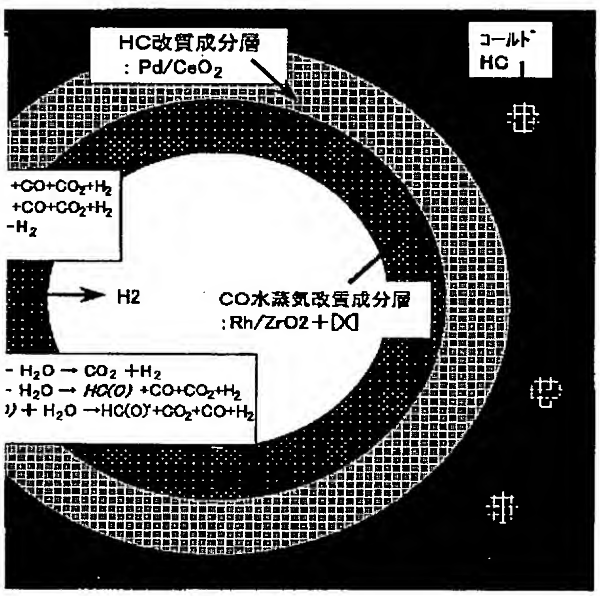
【図５】本発明の排気ガス浄化用触媒の他の例を示す縦断面図である。

【図６】排気ガス浄化用触媒を用いたシステムを示すシステム構成図である。

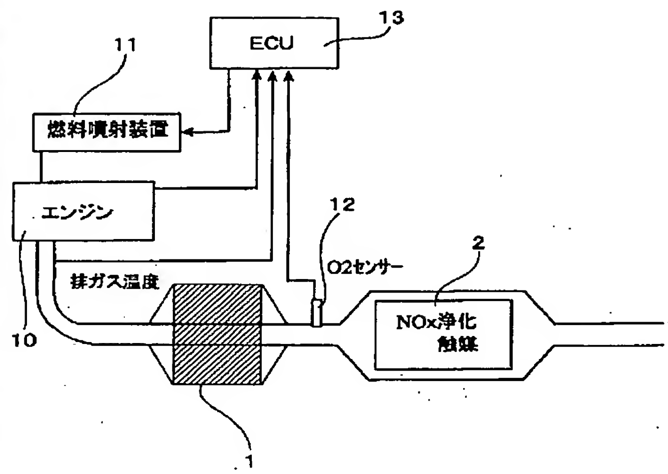
【符号の説明】

１　触媒
２　触媒
１０　エンジン
１１　燃料噴射装置
１２　O_2センサー
１３　ＥＣＵ

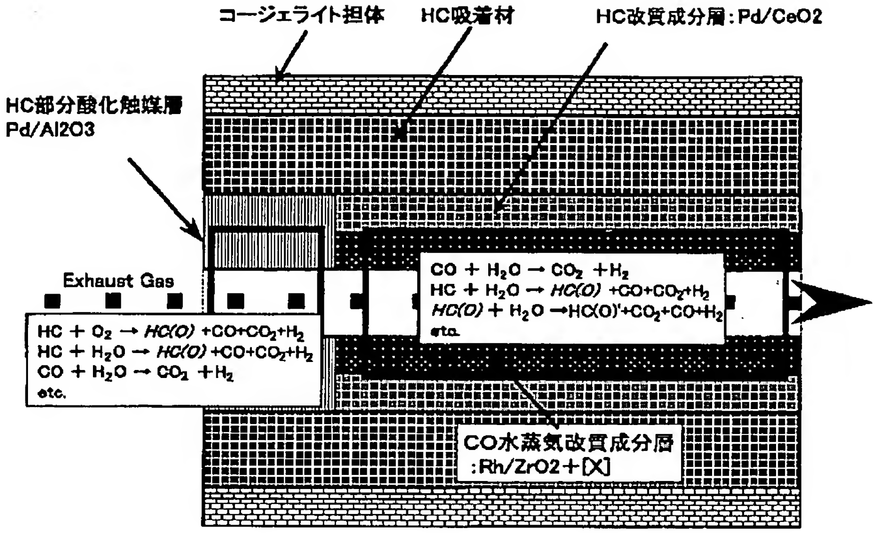
【図１】



【図６】

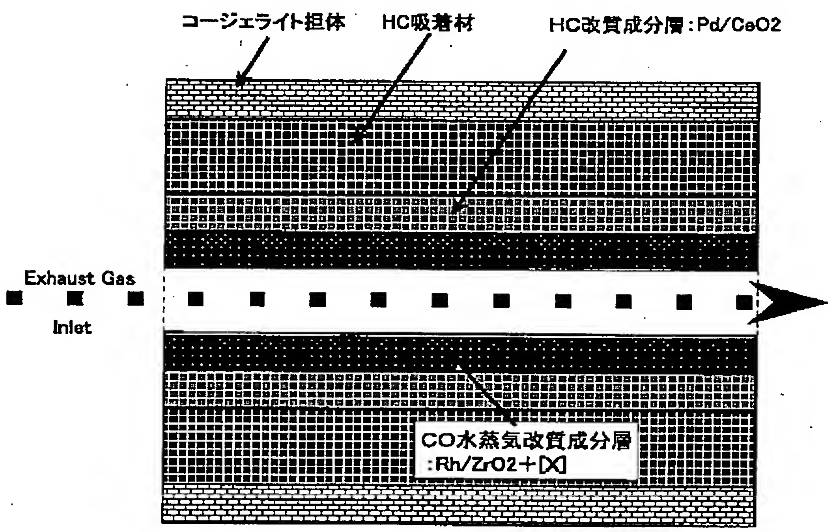


【図２】



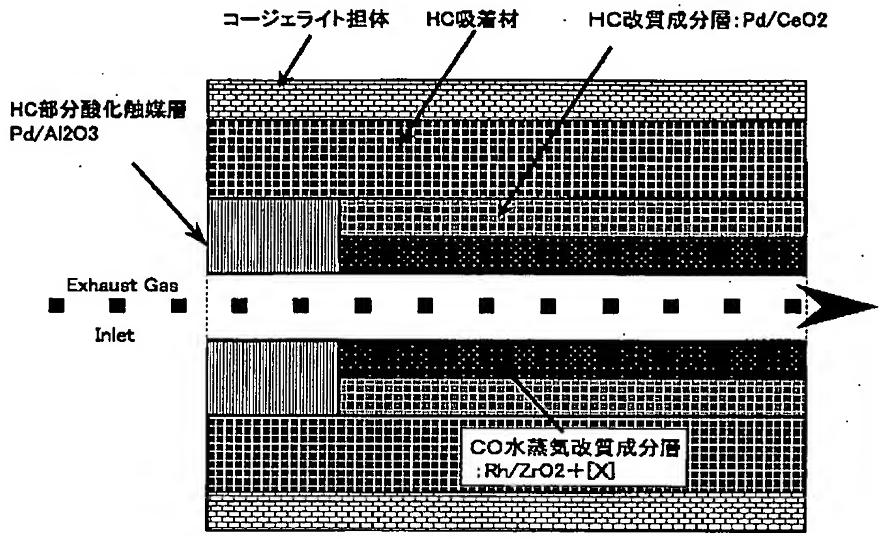
コージェライト担体
HC吸着材
HC改質成分層：Pd/CeO2
HC部分酸化触媒層
Pd/Al2O3
Exhaust Gas
CO + H2O → CO2 + H2
HC + H2O → HC(O) +CO+CO2+H2
HC(O) + H2O →HC(O)'+CO2+CO+H2
etc.
HC + O2 → HC(O) +CO+CO2+H2
HC + H2O → HC(O) +CO+CO2+H2
CO + H2O → CO2 + H2
etc.
CO水蒸気改質成分層
:Rh/ZrO2＋[X]

【図３】

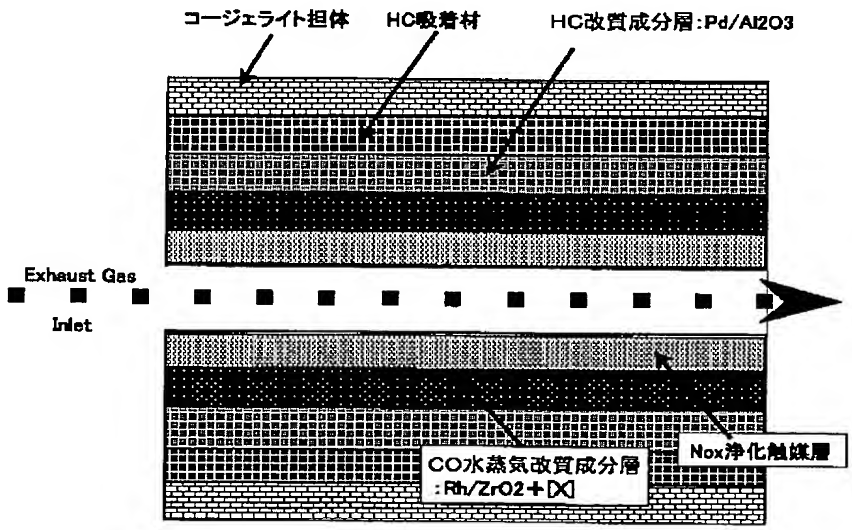


コージェライト担体
HC吸着材
HC改質成分層：Pd/CeO2
Exhaust Gas
Inlet
CO水蒸気改質成分層
:Rh/ZrO2＋[X]

【図４】



【図５】



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BC51B BC71A BC71B BC72A
BC72B BC75A BC75B BD03A
BD07A CA03 CA08 CA10
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ZA04A ZA05A ZA05B ZA06A
ZA11A ZA11B ZA12A ZA19A
ZA19B ZA25A ZA26A ZA30A
ZA31A

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(71)Applicant : NISSAN MOTOR CO LTD
(72)Inventor : YAMAMOTO SHINJI

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(54) EXHAUST GAS CLEANING CATALYST

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an exhaust gas cleaning catalyst with which NOx can be cleaned with high efficiency by using H2 as a reducing agent under an oxygen-excess atmosphere, an HC component and CO component to be not cleaned and discharged in a usual catalyst can be reduced and particularly the HC component can be remarkably reduced in a low temperature region just after an engine is started and which gives highly fuel-efficient effect.
SOLUTION: This catalyst is obtained by layering a zeolite-containing HC adsorbing layer on an integrated structure type carrier and layering a hydrogen generating and nitrogen oxides cleaning catalyst layer, where hydrogen is generated from hydrocarbon and/or carbon monoxide contained in the exhaust gas and nitrogen oxides are cleaned by using the generated hydrogen, on the HC adsorbing layer.

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[Date of requesting appeal against examiner's decision of rejection]	

CLAIMS

[Claim(s)]
[Claim 1] A catalyst for exhaust gas purification which carries out the laminating of the HC adsorption layer on integral-construction mold support, is a catalyst for exhaust gas purification which carries out the laminating of H2 generation and the NOx purification catalyst bed, and changes on this, and is characterized by the above-mentioned H2 generation and NOx purification catalyst bed purifying nitrogen oxides using hydrogen which generated and generated hydrogen from a hydrocarbon and/or a carbon monoxide.
[Claim 2] A catalyst for exhaust gas purification according to claim 1 characterized by to generate hydrogen from a hydrocarbon from which the above-mentioned H2 generation and NOx purification catalyst bed stick to the above-mentioned HC adsorption layer at the time of cold operation of the target internal combustion engine, and is desorbed in a warm-up process, a hydrocarbon discharged after a warm-up of an internal combustion engine, and/or a carbon monoxide, and to purify nitrogen oxides using these hydrogen, carbonization carbon in exhaust gas, and/or a carbon monoxide.
[Claim 3] The above-mentioned H2 generation and NOx purification catalyst bed contain H2 generation catalyst component and an NOx purification catalyst component. The above-mentioned H2 generation catalyst component HC reforming component which reforms a hydrocarbon and generates hydrogen, and CO reforming component which carries out steam reforming of CO and generates hydrogen are contained. The above-mentioned HC reforming component A cerium oxide which supported palladium is contained. The above-mentioned CO reforming component The above-mentioned HC reforming component and the above-mentioned CO reforming component are mixed for the above-mentioned H2 generation and NOx purification catalyst bed by containing a zirconic acid ghost which supported a rhodium, and the same layer is formed, The laminating of the above-mentioned CO reforming component is carried out on the above-mentioned HC reforming component, Or a catalyst for exhaust gas purification according to claim 1 or 2 characterized by consisting of either of the above-mentioned HC reforming component being arranged at the upstream of a flow direction of exhaust gas, and the above-mentioned CO reforming component being arranged at the downstream.
[Claim 4] A catalyst for exhaust gas purification given in any one term of claims 1-3 characterized by including a catalyst bed in which catalyst entrance-side portions of the above-mentioned H2 generation and NOx purification catalyst bed contain an alumina which supported palladium.
[Claim 5] exhaust gas of a catalyst entrance when purifying the above-mentioned nitrogen oxides -- amount of hydrogen/-- all -- a catalyst for exhaust gas purification given in any one term of claims 1-4 characterized by satisfying a gas presentation expressed with amount >=of reduction components 0.3.
[Claim 6] A zirconic acid ghost which supported the above-mentioned rhodium contains alkaline earth metal, and the presentation is degree type **[X] aZrbOc. -- ** (X in a formula) At least one sort of elements chosen from a group which consists of magnesium, calcium, strontium, and barium, and a and b an oxygen atomic number required for a rate of an atomic ratio and c to satisfy a valence of X and Zr -- being shown -- a= 0.01 to 0.5, b= 0.5 to 0.99, and a+b=1 -- filling -- a catalyst for exhaust gas purification given in any one term of claims 3-5 characterized by what is expressed.
[Claim 7] A catalyst for exhaust gas purification given in any one term of claims 4-6 to which at least one catalyst bed chosen from a group which consists of a catalyst bed containing an alumina which supported the above-mentioned HC adsorption layer, a catalyst bed containing the above-mentioned HC reforming component, a catalyst bed containing the above-mentioned CO reforming component, and the above-mentioned palladium is characterized by containing an NOx purification catalyst component.
[Claim 8] At least one catalyst bed chosen from a group which consists of a catalyst bed containing an alumina which supported the above-mentioned HC adsorption layer, a catalyst bed containing the above-mentioned HC reforming component, a catalyst bed containing the above-mentioned CO reforming component, and the above-mentioned

palladium A catalyst for exhaust gas purification given in any one term of claims 4-7 characterized by containing at least one sort of NOx reduction components chosen from a group which consists of palladium, platinum, a rhodium, an alumina, alkali metal, and alkaline earth metal.
[Claim 9] A catalyst for exhaust gas purification according to claim 8 characterized by the above-mentioned alkali metal and/or an alkaline earth metal containing at least one sort of elements chosen from a group which consists of a potassium, caesium, magnesium, calcium, and barium.
[Claim 10] the above-mentioned HC adsorption layer -- Si / 2aluminum ratio -- a catalyst for exhaust gas purification given in any one term of claims 1-9 characterized by containing an H mold beta-zeolite of =10-500.
[Claim 11] A catalyst for exhaust gas purification given in any one term of claims 1-10 characterized by the above-mentioned HC adsorption layer containing at least one sort of zeolites chosen from a group which consists of an H mold beta-zeolite, MFI and Y mold, USY, and mordenite.
[Claim 12] A catalyst for exhaust gas purification according to claim 10 or 11 characterized by a zeolite of the above-mentioned HC adsorption layer containing at least one sort of elements chosen from a group which consists of palladium, magnesium, calcium, strontium, barium, silver, an yttrium, a lanthanum, a cerium, neodymium, Lynn, boron, and a zirconium.

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to the catalyst for emission gas purification, and relates to the catalyst for exhaust gas purification which purifies the nitrogen oxides (NOx) in hyperoxia exhaust gas with a well head in details further.
[0002]
[Description of the Prior Art] Conventionally, the catalyst which performs oxidation of a carbon monoxide (CO) and a hydrocarbon (HC) and reduction of NOx to coincidence is used widely as a catalyst for exhaust gas purification of internal combustion engines, such as an automobile. What added base metal oxides, such as rare earth metals, such as a cerium (Ce) and a lanthanum (La), and nickel (nickel), as a co-catalyst component as such a catalyst if needed [of having made the alumina coat layer on fireproof support supporting noble metals, such as palladium (Pd), and platinum (Pt), a rhodium (Rh), / the thing and if needed] is indicated (JP,58-20307,A). The catalyst currently indicated by the above-mentioned official report is strongly influenced of exhaust gas temperature and an engine setting air-fuel ratio, especially when an internal combustion engine's exhaust gas is hyperoxia, it cannot purify NOx. By carrying out occlusion of NOx to the patent printing No. 2600429 official report, when exhaust gas is hyperoxia, reducing an oxygen density after that and making it a rich ambient atmosphere temporarily as a method of purifying nitrogen oxides, when such an internal combustion engine's exhaust gas is hyperoxia, NOx by which occlusion was carried out is emitted and the method by the so-called rich spike of carrying out purification processing is indicated.
[0003]
[Problem(s) to be Solved by the Invention] however, by the method by rich spike which is indicated in the above-mentioned official report In order to carry out the reduction reaction of NOx under the conditions to which the oxygen density in exhaust gas needed to be periodically reduced also in the operating range of hyperoxia, and the oxygen density fell further A lot of HC and COs as a reducing agent needed to be supplied, and the technical problem that the effect of the improvement in fuel consumption by running by hyperoxia was not fully acquired occurred.
[0004] Furthermore, although a lot of alkali metals and alkaline-earth-metal elements are made to contain in order to carry out occlusion of NOx in a hyperoxia ambient atmosphere for this reason, the oxidation activity at the time of the low temperature of Pt, Pd, and Rh which are an active metal is no longer acquired fully. Moreover, in order to fully purify HC and CO component which were not consumed at an NOx purification reaction, it is necessary to make it purify by oxidation reaction, or to arrange and purify a three way component catalyst in the latter part of an NOx purification catalyst. However, in such a catalyst system, since the catalyst which purifies HC and CO was arranged in the latter part of an exhaust-stream way, sufficient HC and the purification engine performance of CO were not obtained, but the technical problem were difficult also had HC and CO component purification which are discharged especially immediately after engine starting.
[0005] The place which this invention is made in view of the technical problem which such conventional technology has, and is made into the purpose purifies NOx with a well head under a hyperoxia ambient atmosphere, and reduces remarkably HC in HC discharged by un-purifying, CO component, especially the low-temperature region after engine starting, and is to offer the high catalyst for exhaust gas purification of the improvement effect in fuel consumption moreover.
[0006]
[Means for Solving the Problem] That the above-mentioned technical problem should be solved, this invention person came to complete a header and this invention for the above-mentioned technical problem being solvable by performing specific HC reforming processing, CO steam-reforming processing, etc., generating H2, and using these H2 as an NOx

reducing agent, as a result of inquiring wholeheartedly.

[0007] That is, a catalyst for exhaust gas purification of this invention carries out the laminating of the HC adsorption layer on integral-construction mold support, is a catalyst for exhaust gas purification which carries out the laminating of H2 generation and the NOx purification catalyst bed, and changes on this, and is characterized by the above-mentioned H2 generation and NOx purification catalyst bed purifying nitrogen oxides using hydrogen which generated and generated hydrogen from a hydrocarbon and/or a carbon monoxide.

[0008] Moreover, a suitable gestalt of a catalyst for exhaust gas purification of this invention generates hydrogen from a hydrocarbon from which the above-mentioned H2 generation and NOx purification catalyst bed stick to the above-mentioned HC adsorption layer at the time of cold operation of the target internal combustion engine, and is desorb in a warm-up process, a hydrocarbon discharge after a warm-up of an internal combustion engine, and/or a carbon monoxide, and is characterize by to purify nitrogen oxides using these hydrogen, carbonization carbon in exhaust gas, and/or a carbon monoxide.

[0009] Furthermore, other suitable gestalten of a catalyst for exhaust gas purification of this invention The above-mentioned H2 generation and NOx purification catalyst bed contain H2 generation catalyst component and an NOx purification catalyst component. The above-mentioned H2 generation catalyst component HC reforming component which reforms a hydrocarbon and generates hydrogen, and CO reforming component which carries out steam reforming of CO and generates hydrogen are contained. The above-mentioned HC reforming component A cerium oxide which supported palladium is contained. The above-mentioned CO reforming component The above-mentioned HC reforming component and the above-mentioned CO reforming component are mixed for the above-mentioned H2 generation and NOx purification catalyst bed by containing a zirconic acid ghost which supported a rhodium, and the same layer is formed, It is characterized by consisting of either that the laminating of the above-mentioned CO reforming component is carried out on the above-mentioned HC reforming component, or that the above-mentioned HC reforming component is arranged at the upstream of a flow direction of exhaust gas, and the above-mentioned CO reforming component is arranged at the downstream.

[0010] Furthermore, other suitable gestalten of a catalyst for exhaust gas purification of this invention are characterized by including a catalyst bed in which catalyst entrance-side portions of the above-mentioned H2 generation and NOx purification catalyst bed contain an alumina which supported palladium again.

[0011] moreover, exhaust gas of a catalyst entrance in case a suitable gestalt of further others of a catalyst for exhaust gas purification of this invention purifies the above-mentioned nitrogen oxides -- amount of hydrogen/-- all -- it is characterized by satisfying a gas presentation expressed with amount >=of reduction components 0.3.

[0012] Furthermore, other suitable gestalten of a catalyst for exhaust gas purification of this invention again A zirconic acid ghost which supported the above-mentioned rhodium contains alkaline earth metal, and the presentation is degree type **[X] aZrbOc. -- ** (X in a formula) At least one sort of elements chosen from a group which consists of magnesium, calcium, strontium, and barium, and a and b an oxygen atomic number required for a rate of an atomic ratio and c to satisfy a valence of X and Zr -- being shown -- a= 0.01 to 0.5, b= 0.5 to 0.99, and a+b=1 -- filling -- it is characterized by what is expressed.

[0013] Moreover, it is characterized by at least one catalyst bed chosen from a group which consists of a catalyst bed containing an alumina with which other suitable gestalten of a catalyst for exhaust gas purification of this invention supported the above-mentioned HC adsorption layer, a catalyst bed containing the above-mentioned HC reforming component, a catalyst bed containing the above-mentioned CO reforming component, and the above-mentioned palladium containing an NOx purification catalyst component.

[0014] Furthermore, other suitable gestalten of a catalyst for exhaust gas purification of this invention again At least one catalyst bed chosen from a group which consists of a catalyst bed containing an alumina which supported the above-mentioned HC adsorption layer, a catalyst bed containing the above-mentioned HC reforming component, a catalyst bed containing the above-mentioned CO reforming component, and the above-mentioned palladium It is characterized by containing at least one sort of NOx reduction components chosen from a group which consists of palladium, platinum, a rhodium, an alumina, alkali metal, and alkaline earth metal.

[0015] moreover, a suitable gestalt of further others of a catalyst for exhaust gas purification of this invention -- the above-mentioned HC adsorption layer -- Si / 2aluminum ratio -- it is characterized by containing an H mold beta-zeolite of =10-500.

[0016] Furthermore, other suitable gestalten of a catalyst for exhaust gas purification of this invention are characterized by the above-mentioned HC adsorption layer containing at least one sort of zeolites chosen from a group which consists of an H mold beta-zeolite, MFI and Y mold, USY, and mordenite again.

[0017] Moreover, other suitable gestalten of a catalyst for exhaust gas purification of this invention are characterized by

a zeolite of the above-mentioned HC adsorption layer containing at least one sort of elements chosen from a group which consists of palladium, magnesium, calcium, strontium, barium, silver, an yttrium, a lanthanum, a cerium, neodymium, Lynn, boron, and a zirconium.

[0018]

[Embodiment of the Invention] Hereafter, the catalyst for exhaust gas purification of this invention is explained to details. In addition,"%", unless it mentions specially, mass percentage is shown. On integral-construction mold support, the catalyst for exhaust gas purification of this invention carries out the laminating of the HC adsorption layer, on this, carries out the laminating of H2 generation and the NOx purification catalyst bed, and changes.

[0019] A zeolite with cold HC adsorption capacity is used as a principal component, the above-mentioned HC adsorption layer is immediately after the time of cold operation of the target internal combustion engine, i.e., engine starting, when a catalyst is still low temperature, it adsorbs HC, and when it is in a catalyst warming-up process (150-300 degrees C), it is desorbed from HC. Next, by the HC-CO reforming reaction mentioned later, H2 generation and the NOx purification catalyst bed by which the laminating is carried out to the above-mentioned HC adsorption layer can generate H2 from Desorption HC, and can generate H2 further also from HC and/or CO which are discharged at the time of steady operation of an internal combustion engine. These H2 generated often reacts with NOx in exhaust gas as an NOx reducing agent. It is guessed that it can purify efficiently NOx discharged in a catalyst warming-up process until it reaches the operation control of a hyperoxia ambient atmosphere from immediately after engine starting since the reactivity of H2 and NOx is high although temperature does not rise and the NOx purification catalyst component contained in H2 generation and an NOx purification catalyst bed at this time is not fully being activated.

[0020] Generally the above-mentioned HC-CO reforming reaction performed by the above-mentioned H2 generation and NOx purification catalyst bed can be divided into the reforming reaction and CO steam-reforming reaction of HC. This HC reforming reaction Moreover, degree type ** and ** HC+O2 ->HC(O)+CO+CO2+H2 O+H2 -- ** HC+H2 O->HC(O)+CO+CO2+H2 -- It is thought that it is expressed with ** (HC in a formula (O) shows HC after a reforming reaction), and the above-mentioned CO steam-reforming reaction is expressed with degree type **CO+H2 O->CO2+H2 --**.

[0021] It makes it face that the above-mentioned HC-CO reforming reaction generates H2, and the laminating of the above-mentioned H2 generation and NOx purification catalyst bed is carried out on the above-mentioned HC adsorption layer. Although HC reforming component layer which CO reforming component which carries out steam reforming of HC reforming component and CO which reform HC and generate H2, and generates H2 is mixed, and this layer forms one layer, or contains HC reforming component, and CO steam-reforming layer containing CO reforming component form the multilayer by which the laminating is carried out It is desirable to take the structure which carried out the laminating of the CO steam-reforming component layer on HC reforming component layer especially. As shown in drawing 1 , reforming of the HC which the above-mentioned HC adsorption layer was adsorbed and was emitted from the above-mentioned HC adsorption layer in the catalyst warming-up process immediately after engine starting is first carried out to a partial oxidation object, HC (O), and CO and H2 in the above-mentioned HC reforming component layer, and conversion of CO is further carried out to H2 in the above-mentioned CO steam-reforming component layer. Since HC and CO which are contained in exhaust gas in a catalyst warming-up process like **** by taking such structure are reformed and H2 can be generated, also in a hyperoxia operating range, H2 is supplied and after catalyst warming up can carry out purification processing of NOx. In addition, since conversion of the HC should just be carried out in the order of HC reforming reaction and CO steam-reforming reaction, the above-mentioned HC reforming component layer and the above-mentioned CO steam-reforming component layer may take tandem arrangement along exhaust gas passage, and are not limited to especially the above-mentioned multilayer structure.

[0022] Furthermore, it is desirable to make the above-mentioned HC reforming component layer contain the cerium oxide which supported Pd, in order to reform HC and to generate H2, and in order to carry out steam reforming of CO and to generate H2, it is desirable to make the above-mentioned CO steam-reforming component layer contain the zirconic acid ghost which supported Rh. When exhaust gas is passed in the catalyst for emission gas purification of this invention by making these noble metals and oxides contain, it sets in the above-mentioned HC reforming component layer. Mainly Degree type **-** HC+O2 ->HC(O)+CO+CO2+H2 -- ** HC+H2 O->HC(O)+CO+CO2+H2 -- ** CO+H2 O->CO2+H2 -- The reaction of ** occurs and it sets in the above-mentioned CO steam-reforming component layer. Mainly Degree type **, **, and ** CO+H2 O->CO2+H2 -- ** HC+H2 O->HC (O) -- +CO+CO2+H2 --** HC(O) +H -- the reaction of 2 O->HC(O)'+CO2+CO+H2 --** occurs, and while H2 is generated, an exhaust gas component, especially HC and CO are purified.

[0023] Furthermore, when the above-mentioned H2 generation and NOx purification catalyst bed contain not only the above H2 generation catalyst components but an NOx purification catalyst component, while generating H2 which is an

NOx reducing agent with one catalyst again, NOx can be purified efficiently.

[0024] Furthermore, in order to make H2 generate intentionally from HC in exhaust gas, and CO after engine-warm process termination, as for the catalyst for exhaust gas purification of this invention, it is desirable that the catalyst bed in which a part of above-mentioned H2 generation catalyst of the upstream, i.e., this catalyst entrance-side portion, contains the alumina which supported Pd is included. For example, the laminating of the HC partial oxidation catalyst containing Pd support alumina is carried out to the catalyst entrance side on the above-mentioned HC adsorption catalyst bed as one suitable gestalt of the catalyst for exhaust gas purification of this invention, and the structure where the laminating of HC reforming component layer which contains Pd support cerium oxide on the above-mentioned HC adsorption layer, and the CO steam-reforming component layer containing Rh support zirconic acid ghost is carried out is listed to the downstream. Although the above-mentioned structure is shown in drawing 2 , especially the catalyst for emission gas purification of this invention is not limited to this.

[0025] Moreover, as shown in drawing 2 , it sets after catalyst warming up. By the catalyst bed containing the alumina which supported Pd arranged into this above-mentioned catalyst entrance-side portion Conversion of the HC contained by the partial oxidation reaction in exhaust gas is carried out to HC(O) and CO. Next, H2 generation is promoted by the reforming reaction of HC (O) in the above-mentioned HC reforming component layer, and it is guessed that CO2 and H2 are subsequently generated by the steam-reforming reaction from CO and H2O in the above-mentioned CO steam-reforming component layer. Therefore, in this invention, it continues at an above-mentioned catalyst warming-up process, after catalyst warming up can supply H2, and even if it is under a hyperoxia ambient atmosphere, it is thought that the reduction purification of NOx can be carried out.

[0026] thus, instead of [of HC and CO which were mainly used from the former as a reduction component used for NOx purification in the catalyst for exhaust gas purification of this invention] -- or the exhaust gas of the catalyst entrance when ** using H2 being made in addition to this, but carrying out NOx purification further -- H2 amount/-- all -- it is desirable to satisfy the gas presentation expressed with amount >=of reduction components 0.3. If this gas presentation is satisfied, since H2 concentration in exhaust gas will become high, the still higher NOx purification engine performance can be obtained.

[0027] namely, H2 ratio in the exhaust gas at the time of using the exhaust gas and exhaust gas catalyst from an automobile engine conventionally -- H2 amount/-- all -- although it was amount <of reduction components 0.3, the ratio of H2 was low and it was impossible to have used H2 effectively as a reduction component, in this invention, this ratio is increased and H2 is used effectively. in addition, the above-mentioned exhaust gas presentation -- H2 amount/-- all -- although it will come out enough if amount >=of reduction components 0.3 are satisfied -- H2 amount/-- all -- it is still more desirable to be referred to as amount >=of reduction components 0.5.

[0028] Moreover, it is desirable that the above-mentioned Rh support zirconic acid ghost contains alkaline earth metal, and changes in order to maintain the oxidation state of Above Rh in the condition of having been suitable for CO steam-reforming reaction, in the above-mentioned CO steam-reforming component layer, and the presentation is degree type **[X] aZrbOc. -- It is expressed with **. a shows an oxygen atomic number required for the rate of an atomic ratio of this element and b to satisfy the rate of an atomic ratio of Zr, and for c satisfy the valence of this element and Zr by X of the above-mentioned formula ** showing the element concerning the combination of Mg, calcium, Sr or Ba(s), and such arbitration, and a= 0.01 to 0.5, b= 0.5 to 0.99, and a+b=1 are filled. If the above-mentioned alkaline earth metal is made to contain, high catalytic activity can be acquired from the first stage to until after durability.

[0029] Furthermore, as for the catalyst bed concerning the combination of the catalyst beds containing the alumina which supported the above-mentioned HC adsorption layer, the above-mentioned above-mentioned H2 generation and NOx purification catalyst bed, or Above Pd, and such arbitration, it is desirable to contain an NOx purification catalyst component. That is, all of the catalyst bed containing the alumina which supported Pd arranged at the above-mentioned HC adsorption layer, HC reforming component layer, CO steam-reforming component layer, and this catalyst entrance-side portion can be made to contain Pd and Pt which are an NOx purification catalyst component, Rh, etc. While making H2 generate in a catalyst warming-up process by making an NOx purification catalyst component contain, NOx discharged in a catalyst warming-up process can be purified efficiently, and NOx by which after catalyst warming up is discharged at the time of the operation control under a hyperoxia ambient atmosphere can be purified further efficiently. In addition, not only making each catalyst bed contain an NOx purification catalyst component as mentioned above but it may carry out the laminating of the NOx purification catalyst bed further on the above-mentioned H2 generation and NOx purification catalyst bed, and you may carry out the laminating of the NOx purification catalyst bed, without making each catalyst bed contain an NOx purification catalyst component. Furthermore, tandem arrangement of the catalyst for NOx purification may be carried out for the catalyst for emission gas purification of this invention at an emission style side on the street at the downstream.

[0030] Moreover, especially the catalyst bed concerning the combination of the catalyst beds containing the alumina which supported Pd arranged at the above-mentioned HC adsorption layer, HC reforming component layer, CO steam-reforming component layer, or the above-mentioned catalyst entrance-side portion, and such arbitration can contain the NOx purification catalyst component concerning the combination of Pd, Pt, Rh, an alumina, alkali metal or alkaline earth metal, and such arbitration. By containing these NOx purification components, NOx by which it is discharged from an engine from immediately after engine starting till steady operation control of a hyperoxia ambient atmosphere can be purified efficiently. In addition, although the metal concerning the combination of a potassium (K), caesium (Ce), magnesium (Mg), calcium (calcium) or barium (Ba), and such arbitration can be mentioned as the above-mentioned alkali metal and/or an alkaline earth metal, it is not limited to these.

[0031] Furthermore, if the above-mentioned alkali metal and the alkaline-earth-metal content in each above-mentioned whole catalyst bed turn into this 80% of the weight or more of metal content total amount in the catalyst for emission gas purification of this invention, NOx discharged in the Kohl Doreen region is absorbable, but if it becomes less than 80% of the weight, sufficient NOx absorbing power will not be acquired. Moreover, in order for each above-mentioned whole catalyst bed to contain 80% of the weight or more of the total amount of alkali metal and alkaline earth metal, it is desirable that alkali metal and/or alkaline earth metal are insoluble compounds and/or poorly soluble compounds.

[0032] Moreover, although the zeolite used by the above-mentioned HC adsorption layer can be used choosing it suitably from well-known zeolites, it is desirable to choose from ordinary temperature especially what has sufficient HC adsorption capacity and has high endurance even if it is under a water existence ambient atmosphere moreover at a comparatively high temperature. As such a zeolite, typically, Si / 2aluminum ratio is not limited to especially this, although the H mold beta-zeolite of 10-500 is mentioned. Since adsorption inhibition of the moisture with which Si / 2aluminum ratio coexists in exhaust gas in less than ten zeolite is serious, HC cannot be adsorbed effectively but HC adsorption capacity may fall in the zeolite with which Si / 2aluminum ratio exceeds 500.

[0033] Furthermore, according to the exhaust gas component discharged from an engine, the zeolite concerning the combination of MFI and Y mold with which pore size differs from pore structure, USY or mordenites, and such arbitration is chosen, and if it mixes and uses for the above-mentioned H mold beta-zeolite, HC in exhaust gas can be adsorbed efficiently.

[0034] In addition, although it has HC adsorption capacity sufficient also with the above-mentioned H mold beta-zeolite To the various above-mentioned zeolites, Pd, Mg, calcium, strontium (Sr), Ba, silver (Ag), an yttrium (Y), La and Ce, neodymium (Nd), HC adsorbent ability and HC desorption control ability can be further improved by supporting the element concerning the combination of Lynn (P), boron (B) or zirconiums (Zr), and such arbitration using the usual methods, such as an ion-exchange method, an impregnation method, and dip coating.

[0035] Moreover, there is for example, honeycomb support in the up Norikazu object structured type catalyst support of the catalyst for exhaust gas purification of this invention, and, generally many things of quality of cordierite, such as a ceramic, are used for it as a honeycomb material. However, it may not be restricted to this, but the honeycomb material which consists of metallic materials, such as ferrite system stainless steel, may be used, and the catalyst component powder itself may be further fabricated in a honeycomb configuration.

[0036]

[Example] Hereafter, although an example and the example of a comparison explain this invention to details further, this invention is not limited to these examples.

[0037] It sank into cerium oxide (CeO2) powder, the [preparation of catalyst powder of HC reforming component layer] nitric-acid Pd aqueous solution was dried and calcinated, and Pd support cerium oxide powder A was obtained. Pd support concentration of this powder was 10%. Moreover, what set to Powder D and Zr0.9Ce 0.1O2 what set to Powder C and Zr0.5Ce 0.5O2 what used as Powder B the powder which repeated and obtained the same actuation as Powder A, and set it to Zr0.2Ce 0.8O2 was used as Powder E except having been referred to as Zr0.1Ce 0.9O2 instead of CeO2. Furthermore, the powder which repeated and obtained the same actuation as Powder A was used as Powder F except having made Pd support concentration into 5%.

[0038] It sank into calcium0.2Zr0.8O2 powder, the [preparation of catalyst powder of CO steam-reforming component layer] nitric-acid Rh aqueous solution was dried and calcinated, and Rh support zirconic acid ghost powder G was obtained. Rh support concentration of this powder was 6%. Instead of calcium0.2Zr 0.8O2 moreover, except having been referred to as Mg0.1Zr 0.9O2 What used as Powder H the powder which repeated and obtained the same actuation as Powder G, and was set to Ba0.1Zr 0.9O2 Powder I What set to Powder J and calcium0.1Mg0.1Zr 0.8O2 what was set to Sr0.2Zr 0.8O2 Powder K What set to Powder M and calcium0.5Zr 0.5O2 what set to Powder L and calcium0.01Zr 0.99O2 what was set to calcium0.1Ba0.05Mg0.05Zr 0.8O2 was used as Powder N.

[0039] It sank into activated-alumina (aluminum 2O3) powder, the [preparation of catalyst powder of catalyst bed

containing alumina which supported Pd] nitric-acid Pd aqueous solution was dried and calcinated, and Pd support alumina powder O was obtained. Pd support concentration of this powder was 15%. Moreover, except having been referred to as aluminum 2O3 which contains Ce 3% instead of aluminum 2O3 What set what set what used as Powder P the powder which repeated and obtained the same actuation as Powder O, and was set to aluminum 2O3 which contains Zr 3% to aluminum 2O3 which contains Powder Q and La 3% to aluminum 2O3 which contains Powder R and Zr 10% was used as Powder S.

[0040] It sank into aluminum2O3 powder, the [preparation of catalyst powder containing NOx purification catalyst component] nitric-acid Pd aqueous solution was dried and calcinated, and Pd support alumina powder T was obtained. Pd support concentration of this powder T was 8%. It sank into 2Oaluminum3 powder, the dinitrodiammine Pt acid aqueous solution was dried and calcinated, and Pt support alumina powder U was obtained. Pt support concentration of this powder U was 6%. It sank into 2Oaluminum3 powder, the nitric-acid Rh aqueous solution was dried and calcinated, and Rh support alumina powder V was obtained. Rh support concentration of this powder V was 4%.

[0041] After having carried out preferential grinding of [catalyst preparation 1] beta-zeolite (Si/2aluminum=25) 900g, silica sol 100g, and the 1000g of the pure water, having made it into the slurry, making it adhere to the nature monolith support of cordierite (900 cels / 4 mils, 1.3L) and drying and calcinating it, the zeolite catalyst of amount of zeolite coats 100 g/L was acquired. Subsequently, carried out preferential grinding of the 800g of the pure water to powder A706g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to a zeolite catalyst, and dried and calcinated, and the catalyst A which carried out the coat of 72 g/L to the zeolite catalyst was acquired. The amount of Pd support of this catalyst A was 7.06g./L. Furthermore, carried out preferential grinding of the 600g of the pure water to powder G588g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to Catalyst A, and dried and calcinated, and the catalyst AG1 which carried out the coat of 60 g/L to Catalyst A was acquired. The amount of Rh support of this catalyst AG1 was 3.53 g/L. The catalyst AG1 was made into 3 layer structures shown in drawing 3 . Moreover, a repeat and catalysts 2-AG 7 were acquired for the same actuation using HC adsorption material shown in a table 2 instead of beta-zeolite (Si/2aluminum=25).

[0042] Carried out preferential grinding of the 800g of the pure water to [catalyst preparation 2] powder B706g and nitric-acid nature alumina binder 14g, considered as the slurry, and it was made to adhere to the zeolite catalyst which repeated and prepared the same actuation as catalyst preparation 1, and dried and calcinated, and the catalyst B which carried out the coat of 72g / the L to the zeolite catalyst was acquired. The amount of Pd support of this catalyst B was 7.06 g/L. Next, carried out preferential grinding of the 600g of the pure water to powder G588g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to Catalyst B, and dried and calcinated, and the catalyst BG which carried out the coat of 60 g/L to Catalyst B was acquired. The amount of Rh support of this catalyst BG was 3.53 g/L. Catalyst BG was made into 3 layer structures shown in drawing 3 . Moreover, powder C-F was used instead of Powder B, the same actuation was repeated, and Catalysts CG, DG, EG, and FG were acquired.

[0043] The repeat and the zeolite catalyst were acquired for the same actuation as catalyst preparation 1 except having considered as HC adsorption material shown in a table 2 instead of the [catalyst preparation 3] beta-zeolite (Si/2aluminum=25). Next, carried out preferential grinding of the 1500g of the pure water to powder B706g, powder A706g, and nitric-acid nature alumina binder 28g, considered as the slurry, and it was made to adhere to a zeolite catalyst, and dried and calcinated, and the catalyst BA which carried out the coat of 144 g/L to the zeolite catalyst was acquired. The amount of Pd support of this catalyst BA was 14.12 g/L. Furthermore, carried out preferential grinding of the 600g of the pure water to powder H588g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to Catalyst BA, and dried and calcinated, and the catalyst BAH which carried out the coat of 60 g/L to Catalyst BA was acquired. The amount of Rh support of this catalyst BAH was 3.53 g/L. Catalyst BAH was made into 3 layer structures shown in drawing 3 . Moreover, powder I-N was used instead of Powder H, the same actuation was repeated, and Catalysts BAI, BAJ, BAK, BAL, BAM, and BAN were acquired.

[0044] After having carried out preferential grinding of [catalyst preparation 4] beta-zeolite (Si/2aluminum=25) 900g, silica sol 100g, and the 1000g of the pure water, having made it into the slurry, making it adhere to the nature monolith support of cordierite (900 cels / 4 mils, 1.3L) and drying and calcinating it, the zeolite catalyst of amount of zeolite coats 50 g/L was acquired. Carried out preferential grinding of the 500g of the pure water to powder O471g and nitric-acid nature alumina binder 9g, considered as the slurry, this was made to adhere to 1/4 portion of the exhaust gas entrance side of a zeolite catalyst, it dried and calcinated, and the catalyst O1 which carried out the coat of 48 g/L to the zeolite catalyst was acquired. The amount of Pd support of this catalyst O1 was 7.06 g/L. Subsequently, it was made to adhere to 3/4 portion which carries out preferential grinding of the 1000g of the pure water to powder B706g, powder A706g, and nitric-acid nature alumina binder 28g, considers as a slurry, and has not carried out the coat of the catalyst O1, and dried and calcinated, and the catalyst OBA which carried out the coat of 144 g/L was acquired. The total amount of Pd

support of this catalyst OBA was 21.18 g/L. Furthermore, it was made to adhere to 3/4 portion which carries out preferential grinding of the 600g of the pure water to powder L588g and nitric-acid nature alumina binder 12g, considers as a slurry, and has not carried out the coat of the catalyst O1, and dried and calcinated, and the catalyst OBAL which carried out the coat of 60 g/L to Catalyst OBA was acquired. The amount of Rh support of this catalyst OBAL was 3.53 g/L. Catalyst OBAL was made into the structure shown in drawing 4 . Moreover, the zeolite catalyst of amount of zeolite coats 50 g/L was created using HC adsorption material shown in a table 2 instead of beta-zeolite (Si/2aluminum=25), instead of Powder O, powder B-F was used instead of Powder A, powder G-K was used for P-S instead of Powder L, the same actuation was repeated, and Catalysts PBBK, QBCJ, and RBDI, SBEH, and OBFG were obtained.

[0045] Carried out preferential grinding of the 1000g of the pure water to [catalyst preparation 5] powder B706g and nitric-acid nature alumina binder 14g, considered as the slurry, and it was made to adhere to the zeolite catalyst which repeated and obtained the same actuation as the catalyst preparation 4, and dried and calcinated, and catalyst B-2 which carried out the coat of 72 g/L was obtained. The amount of Pd support of this catalyst B-2 was 7.06 g/L. Subsequently, carried out preferential grinding of the 600g of the pure water to powder G588g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to catalyst B-2, and dried and calcinated, and the catalyst BG which carried out the coat of 60 g/L to catalyst B-2 was acquired. The amount of Rh support of this catalyst BG was 3.53 g/L. Furthermore, carry out barium acetate by Na2O conversion, carry out preferential grinding of 20g, nitric-acid nature alumina binder 14g, and the 1500g of the pure water to 20g by BaO conversion, make powder T618g, powder U530g, powder V88g, and a sodium hydroxide into a slurry, and they were made to adhere to Catalyst BG, it dried and calcinated and the catalyst BGN1 which carried out the coat of 147 g/L to Catalyst BG was acquired. The amount of Pd support of this catalyst BGN1 was [3.18 g/L and the amount of Rh support of 12.0 g/L and the amount of Pt support] 3.88 g/L. The catalyst BGN1 was made into the structure shown in drawing 5 .

[0046] [Preparation of catalyst for NOx purification] powder T618g, and powder U530g, 20g and barium acetate by BaO conversion by Na2O conversion for powder V88g and a sodium hydroxide 20g, Carried out preferential grinding of the 1500g of the pure water to nitric-acid nature alumina binder 14g, considered as the slurry, and it was made to adhere to the nature monolith support of cordierite (400 cels / 6 mils, 1.3L), and dried and calcinated, and the catalyst N1 which carried out the coat of 147 g/L was acquired. The amount of Pd support of this catalyst N1 was [3.18 g/L and the amount of Rh support of 4.94 g/L and the amount of Pt support] 0.35 g/L. The catalyst N1 was made into monolayer structure. Moreover, magnesium acetate was used instead of the sodium hydroxide, the same actuation was repeated, and the catalyst N2 was acquired for the catalyst which supported 10 g/L as MgO and supported 10 g/L as BaO.

[0047] Carry out preferential grinding of 10g, nitric-acid nature alumina binder 9g, and the 1000g of the pure water by BaO conversion, make [preparation of three way component catalyst] powder T565g, powder F226g, and barium acetate into a slurry, and they were made to adhere to the nature monolith support of cordierite (900 cels / 2 mils, 1.3L), it dried and calcinated and the catalyst T0 which carried out the coat of 90 g/L was acquired. Furthermore, carried out preferential grinding of the 500g of the pure water to powder V128g and 200g of 0.8OCe0.2Zr2 powder, and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to a catalyst T0, and dried and calcinated, and the catalyst T1 of the two-layer structure which carried out the coat of 34 g/L to the catalyst T0 was acquired. 5.65 g/L and the amount of Rh support of the amount of Pd support of this catalyst T1 were 0.51 g/L.

[0048] The main catalyst components of each above-mentioned catalyst powder etc. were shown in the [catalyst specification] table 1, and the specification of the catalyst created by each above-mentioned catalyst preparation was shown in a table 2.

[0049]

[A table 1]

触媒粉末	担持貴金属種 (−)	担持濃度 (%)	担持基材
A	Pd	10.0	CeO_2
B	Pd	10.0	$Zr_{0.1}Ce_{0.9}O_2$
C	Pd	10.0	$Zr_{0.2}Ce_{0.8}O_2$
D	Pd	10.0	$Zr_{0.5}Ce_{0.5}O_2$
E	Pd	10.0	$Zr_{0.9}Ce_{0.1}O_2$
F	Pd	5.0	CeO_2
G	Rh	6.0	$Ca_{0.2}Zr_{0.8}O_2$
H	Rh	6.0	$Mg_{0.1}Zr_{0.9}O_2$
I	Rh	6.0	$Ba_{0.1}Zr_{0.9}O_2$
J	Rh	6.0	$Sr_{0.2}Zr_{0.8}O_2$
K	Rh	6.0	$Ca_{0.1}Mg_{0.1}Zr_{0.8}O_2$
L	Rh	6.0	$Ca_{0.1}Ba_{0.05}Mg_{0.05}Zr_{0.8}O_2$
M	Rh	6.0	$Ca_{0.01}Zr_{0.99}O_2$
N	Rh	6.0	$Ca_{0.5}Zr_{0.5}O_2$
O	Pd	15.0	Al_2O_3
P	Pd	15.0	Ce3%-Al_2O_3
Q	Pd	15.0	Zr3%-Al_2O_3
R	Pd	15.0	La3%-Al_2O_3
S	Pd	15.0	Zr10%-Al_2O_3
T	Pd	8.0	Al_2O_3
U	Pt	6.0	Al_2O_3
V	Rh	4.0	Al_2O_3

[0050]
[A table 2]

触媒	触媒構造	貴金属担持量(g/L) Pd	Pt	Rh	(g/L) アルカリ	(g/L) アルカリ土類	HC吸着材層	第一層	第二層	第三層
AG1	図3	7.06	—	3.53	—	—	β(Si/2Al=25)	A	G	—
AG2	図3	7.06	—	3.53	—	—	β(Si/2Al=15)	A	G	—
AG3	図3	7.06	—	3.53	—	—	β(Si/2Al=300)	A	G	—
AG4	図3	7.06	—	3.53	—	—	β(=25)+ZSM5(30)	A	G	—
AG5	図3	7.06	—	3.53	—	—	β(=25)+USY(=15)	A	G	—
AG6	図3	7.06	—	3.53	—	—	AgP−β(=25)	A	G	—
AG7	図3	7.06	—	3.53	—	—	Pd−β(=25)	A	G	—
BG	図3	7.06	—	3.53	—	—	β(=25)	B	G	—
CG	図3	7.06	—	3.53	—	—	β(=25)	C	G	—
DG	図3	7.06	—	3.53	—	—	β(=25)	D	G	—
EG	図3	7.06	—	3.53	—	—	β(=25)	E	G	—
FG	図3	7.06	—	3.53	—	—	β(=25)	F	G	—
BAH	図3	14.12	—	3.53	—	—	β(=25)	B+A	H	—
BAI	図3	14.12	—	3.53	—	—	β(=25)	B+A	I	—
BAJ	図3	14.12	—	3.53	—	—	β(=25)	B+A	J	—
BAK	図3	14.12	—	3.53	—	—	β+ZSM5	B+A	K	—
BAL	図3	14.12	—	3.53	—	—	β+USY	B+A	L	—
BAM	図3	14.12	—	3.53	—	—	AgP−β	B+A	M	—
BAN	図3	14.12	—	3.53	—	—	Pd−β	B+A	N	—
OBAL	図4	21.18	—	3.53	—	—	β	O	B+A	L
PBBK	図4	21.18	—	3.53	—	—	β	P	2×B	K
QBCJ	図4	21.18	—	3.53	—	—	β+ZSM5	Q	B+C	J
RBDI	図4	21.18	—	3.53	—	—	β+USY	R	B+D	I
SBEH	図4	21.18	—	3.53	—	—	AgP−β	S	B+E	H
OBFG	図4	21.18	—	3.53	—	—	Pd−β	O	B+F	G
BGN1	図5	12.0	3.18	3.88	$(Na_2O)_2$	$(BaO)_{20}$	β	B	G	T+U+V
N1	単一層	4.94	3.18	0.35	$(Na_2O)_2$	$(BaO)_{20}$				
N2	単一層	4.94	3.18	0.35	$(MgO)_{10}$	$(BaO)_{10}$				
T1	単一層	5.65	—	0.51	—	$(BaO)_{10}$				

[0051] The <performance evaluation of each catalyst> performance evaluation performed vehicles evaluation, and measured the discharge of each exhaust gas component when running in the FTP-75 mode (LA-4) which is a static test mode in North America. The exhaust gas purification structure of a system used for this performance evaluation is shown in drawing 6 . This system consists of catalysts 1 and 2, an engine 10, a fuel injection equipment 11, O2 sensor 12, and ECU13. On vehicles, the catalyst shown in a table 3 at the catalyst 1 by the side of an emission style on the street has been arranged, N1 which is the above-mentioned catalyst for NOx purification, or N2 has been arranged for the catalyst 2 of the downstream, and it considered as examples 1-30 and the example 1 of a comparison. the above-mentioned system purified exhaust gas and the survival rate of HC, CO, and NOx was investigated in the formula expressed with degree type ** survival rate ={1-(HC [in the exhaust gas of an NOx purification catalyst outlet], CO, NOx discharge)/(HC [in the exhaust gas of an engine out], CO, NOx discharge)} x100(%) --** (HC in the above-mentioned exhaust gas, CO, and an NOx discharge show the discharge when running the above-mentioned vehicles evaluation mode). Moreover, a table 3 is the value calculated using the transit portion immediately after the start in the case of running in the above-mentioned vehicles evaluation mode, NOx of the portion specifically excluding after the start in the FTP-75 mode, and the transit portion by about 200 seconds, and the average concentration of each component of HC. Moreover, HC concentration was similarly calculated using average concentration. Non-burned HC

is discharged immediately after an engine start, and HC concentration of having removed the transit portion immediately after a start is because it becomes high and cannot evaluate correctly. In addition, the performance evaluation was performed on the conditions shown below.
[0052]
(Durable conditions)
Engine displacement 3000 cc Fuel The Nippon Oil dash gasoline (Pb=0 mg/usg, S= 30 ppm or less)
Catalyst inlet gas temperature 650 degrees C Durable time amount 50 hours [0053]
(Performance-evaluation conditions)
Catalyst capacity Catalyst 1: Catalyst of this invention 1.3L Catalyst 2:NOx purification catalyst 1.3L Evaluation vehicles Nissan Motor Co., Ltd. make Direct injection 1.8L engine [0054] The obtained result was shown in a table 3.
[0055]
[A table 3]

	搭載 位置		残存率 (%)		
	1 触媒	2 触媒	HC	CO	NOx
実施例1	AG1	N1	1.3	1.9	2.4
実施例2	AG2	N1	1.2	1.8	2.2
実施例3	AG3	N1	1.1	1.7	2.1
実施例4	AG4	N1	1.1	1.8	1.9
実施例5	AG5	N1	1.2	1.8	2.0
実施例6	AG6	N1	1.2	1.7	2.0
実施例7	AG7	N1	1.2	1.8	2.1
実施例8	BG	N1	1.2	1.7	1.9
実施例9	CG	N1	1.3	1.6	2.1
実施例10	DG	N1	1.3	1.6	2.2
実施例11	EG	N1	1.2	1.7	2.0
実施例12	FG	N1	1.2	1.8	2.1
実施例13	BAH	N1	1.1	1.9	1.9
実施例14	BAI	N1	1.1	1.8	1.9
実施例15	BAJ	N1	1.1	1.8	2.0
実施例16	BAK	N1	1.2	1.8	2.0
実施例17	BAL	N1	1.1	1.9	2.1
実施例18	BAM	N1	1.2	1.8	2.1
実施例19	BAN	N1	1.3	1.8	2.2
実施例20	OBAL	N1	1.4	2.0	2.2
実施例21	PBBK	N1	1.2	1.8	2.1
実施例22	QBCJ	N1	1.1	1.9	1.9
実施例23	RBDI	N1	1.1	1.8	1.9
実施例24	SBEH	N1	1.1	1.8	2.0
実施例25	OBFG	N1	1.2	1.8	2.0
実施例26	BGN1	N1	1.3	2.4	2.2
実施例27	AG1	N2	1.2	1.7	2.0
実施例28	BG1	N2	1.3	1.6	2.1
実施例29	BAH	N2	1.2	1.7	2.1
実施例30	OBFG	N2	1.1	1.8	2.0
比較例1	T1	N1	4.2	7.1	7.3

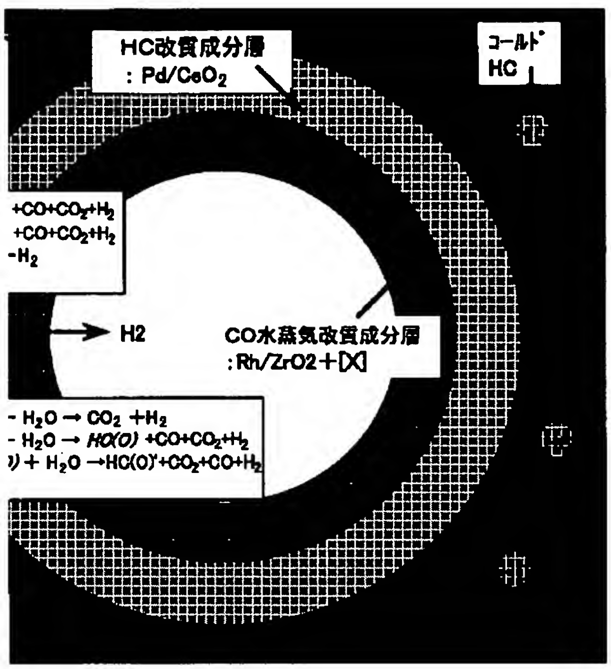
[0056]
[Effect of the Invention] As mentioned above, by according to this invention, performing specific HC reforming processing, CO steam-reforming processing, etc., generating H2, and using these H2 as an NOx reducing agent, as explained Under a hyperoxia ambient atmosphere, it can be efficient, and NOx can be purified by using H2 as a

reducing agent, and HC in HC discharged by un-purifying, CO component, especially the low-temperature region after engine starting can be reduced remarkably, and, moreover, the high catalyst for exhaust gas purification of the improvement effect in fuel consumption can be offered.

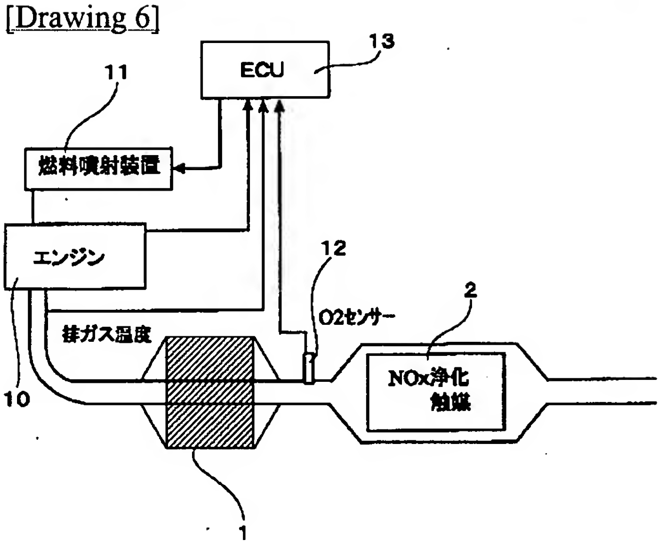
[Translation done.]

DRAWINGS

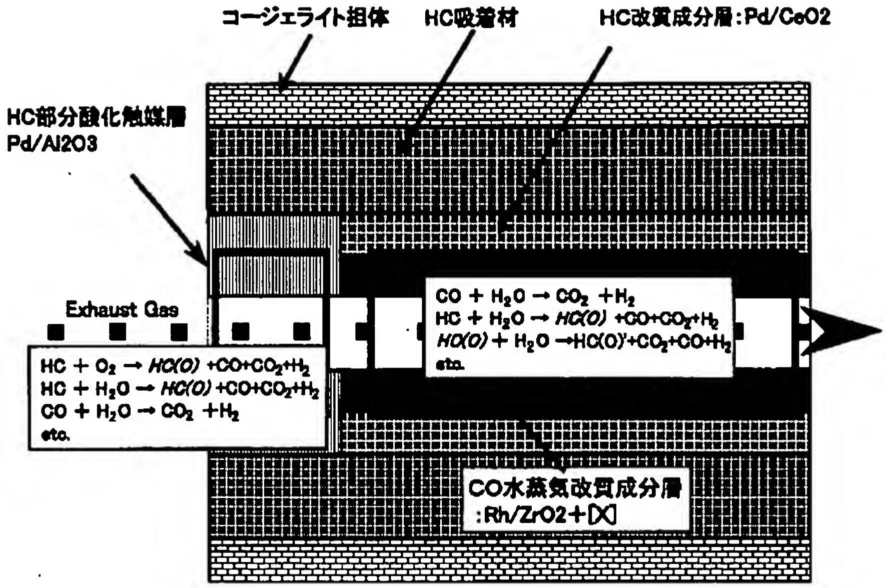
[Drawing 1]



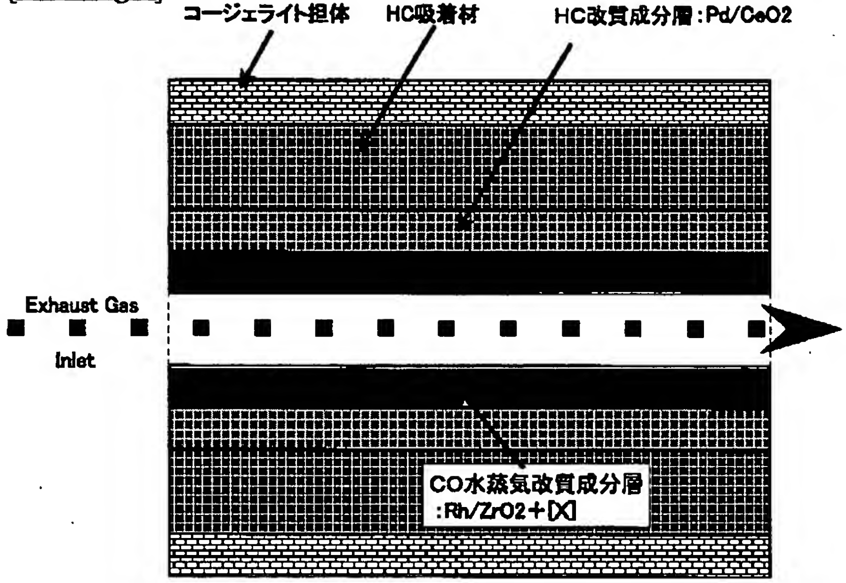
[Drawing 6]



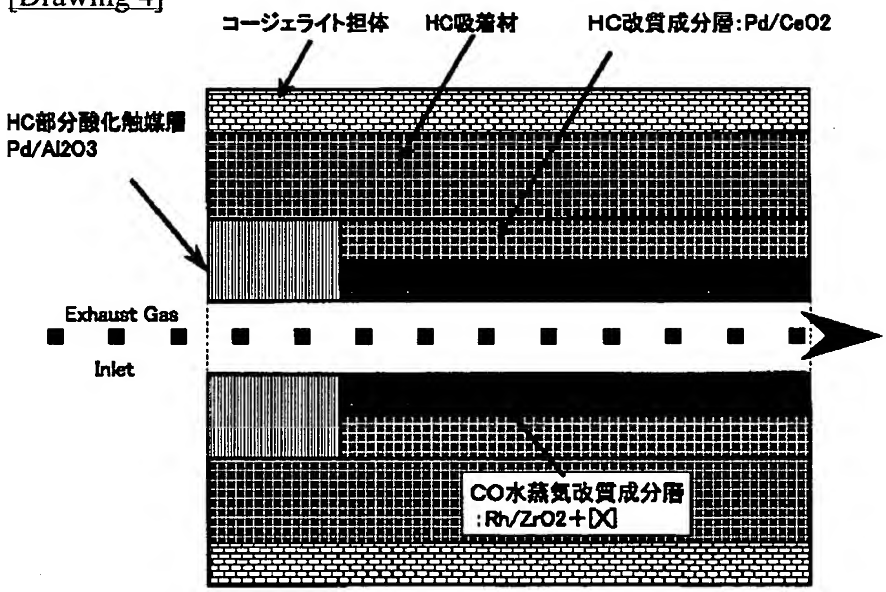
[Drawing 2]



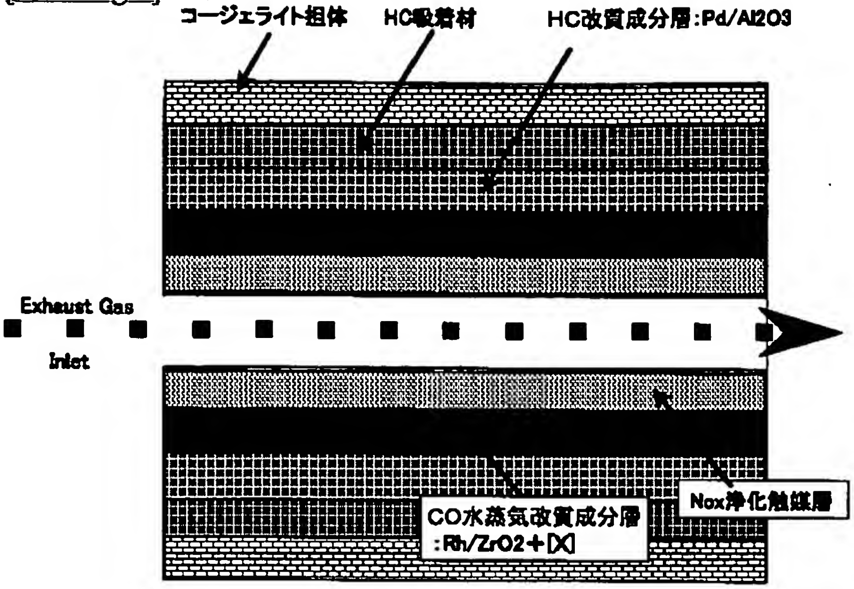
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]